SPIN POLARIZED DENSITY FUNCTIONAL THEORY APPLIED TO THE STUDY OF NANOALLOYS

Erlinda del V. Ortiz[a,b], María B. López[a] and Eduardo A. Castro[c]

[a] *Centro de Investigaciones Fisicoquímicas, Teóricas y Aplicadas (CIFTA), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Catamarca, Av. Belgrano 300, 4700, Catamarca, Argentina, valleortiz@yahoo.com.ar*

[b] *Facultad de Tecnología y Ciencias Aplicadas, Universidad Nacional de Catamarca, Maximio Victoria 55, 4700, Catamarca, Argentina*

[c] *Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas, CONICET, Universidad Nacional de la Plata, Diag. 113 y 64, Suc.4, C.C. 16, 1900, La Plata, Argentina*

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Abstract. The electronic properties and reactivity of Ag_xPt_{10-x}. ($1 \leq x \leq 10$) nanoalloys were investigated by spin polarized calculations within the framework of density-functional theory (SP-DFT). Both the most energetically stable structures and the most reactive nanoalloys were determined through global reactivity indicators: chemical potential and chemical hardness. Our results revealed that the energy stability of nanoalloys increased with the number of Pt-Pt interactions, while the Ag6Pt4 structure was the most reactive of the series under study.

1   INTRODUCTION

In materials science, the range of properties of metallic systems can be greatly extended by taking mixtures of elements to generate intermetallic compounds and alloys. In many cases, there is an enhancement in specific properties upon alloying due to synergistic effects, and the rich diversity of compositions, structures, and properties of metallic alloys has led to widespread applications in electronics, engineering, and catalysis. The desire to fabricate materials with well defined, controllable properties and structures on the nanometer scale coupled with the flexibility afforded by intermetallic materials has generated interest in bimetallic and trimetallic nanoclusters, which will be referred to as alloy nanoclusters or nanoalloys (Jellinek and Krissinel, 1997; Ferrando et al., 2008).

One of the major reasons for interest in nanoalloys is the fact that their chemical and physical properties may be tuned by varying the composition and atomic ordering as well as the size of the clusters. In fact, nanoalloys may display not only magic sizes but also magic compositions, i.e., compositions which present a special stability (Baletto and Ferrando, 2005).

Nanoalloys are also of interest as they may display structures and properties which are distinct from those of the pure elemental clusters: the structures of binary clusters may be quite different from the structures of the corresponding pure clusters of the same size; synergism is sometimes observed in catalysis by bimetallic nanoalloys. They may also display properties which are distinct from the corresponding bulk alloys due to finite size effects, e.g., there are examples of pairs of elements (such as iron and silver) which are immiscible in the bulk but readily mix in finite clusters (Andrews and O´Brien, 1992).

An interesting case is the Silver (Ag)-Platinum (Pt) system. In the bulk, Ag–Pt bimetallic system has a large miscibility gap at the temperature below about 1190 °C (Massalski, et al., 1986) and forms alloys only at very high atomic content of either Ag or Pt (Rhines, 1956). When the atomic composition falls outside the range between Ag_2Pt_{98} and $Ag_{95}Pt_5$ at 400 º C, the bulk materials exist in more than one phase: one Pt-enriched and the other Ag-enriched alloy. However, Peng and Yang (Peng and Yang, 2008) have reported recently Ag-Pt alloy nanoparticles with composition through the entire miscibility gap of the bulk, that were successfuly synthesized in a non-hydrolytic organic colloidal system. The lattice parameter and composition of these nanoparticles were experimentally determined and their relationship followed the Vegard´s law, a strong indication of the alloy formation between platinum and silver at nanometer scale.

Paz Borbón et al. (Paz Bordón et al., 2008) have studied through a combined empirical-potential (EP)/density functional method structural motifs, mixing and segregation effects in 38-atom binary clusters of element from group 10 and 11 of the Periodic Table, composed of the four pairs: Pt-Ag, Ag-Au, Pd-Au and Ag-Pt (Paz Bordón et al., 2008). The results have confirmed that mixed five-fold-symmetric/close-packed or decahedral arrangements are favored for the Pt-Pd, Ag-Pt and Ag-Au pairs. To our knowledge no other theoretical study has reported on the electronic and structural properties of Ag-Pt nanoalloy.

In this paper, using the first-principles methods based on the spin polarized density functional theory (SP-DFT) (Pant and Rajagopal, 1972), we investigated the equilibrium geometries and electronic properties through reactivity descriptors in the series of Ag_xPt_{10-x} (1 $\leq$ x $\leq$ 10). Global l reactivity descriptors, such as chemical potential and chemical hardness, were used to determine the reactivity in the bimetallic nanoalloys.

2   THEORETICAL BACKGROUND

Density functional theory (DFT) (Parr and Yang, 1989) is not only one of today's most powerful computational tools in quantum chemistry and solid-state physics, but it provides a natural background for the definition of a wide range of chemical reactivity descriptors, which field of research is called conceptual DFT. DFT's power lies in the use of the electron density $\rho(r)$ as the basic variable in the description of electron systems in a scalar external potential $v(r)$, instead of the complicated many-electron wavefunction $\Psi(r_1,s_1,...r_n,s_n)$.

In this representation the cardinal reactivity descriptors are electronegativity (Sen and Jorgensen, 1987), χ, and hardness (Sen, 1987; Pearson, 1997), η. They are defined as the following first (Parr et al., 1978) and second (Parr and Pearson, 1983) derivatives of energy, E, with respect to N, at $v(r)$ is fixed,

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)}$$

(1)

and

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)}$$

(2)

where μ is the chemical potential (Parr et al., 1978).

Local reactivity descriptors are neend to explain the site selectivity in a cluster. The most widely used local descriptor is the Fukui function defined as (Parr and Yang, 1984)

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)}\right)_N$$

(3)

From the discontinuity in the $\rho(r)$ versus N curve, three different derivatives are usually defined,

$$f^\xi(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^\xi_{v(r)}$$

(4)

where the superscript $\xi = +$, - or 0, allows to have three different types of Fukui function, viz. $f^-(r)$ for electrophilic attack, $f^+(r)$ for nucleophilic attack and f o(r) for radical attack.

DFT has also been extended to embrace systems that are influenced by a magnetic external field B(r) as well, the most elementary extension being the so-called spin polarized density functional theory (SP-DFT) where magnetic fields act only on the spins of the electrons and the dipolar interaction between spins is excluded. Furthemore, if the limit of the magnetic flux density B→0, the formalism leads to a suitable description of the electronic structure of atoms with a spin-polarized ground state without an external magnetic field , naturally.

The electron density, $\rho(r)$, and the spin density, $\rho_s(r)$, are defined in terms of the spin-α and spin-β populations as,

$$\rho(r) = \rho_\alpha(r) + \rho_\beta(r) \quad \text{and} \quad \rho_S(r) = \rho_\alpha(r) - \rho_\beta(r)$$

(5)

In an orbital formulation, like the Kohn-Sham approach (Kohn and Sham, 1965) these spin densities are written in terms of the corresponding orbital densities as,

$$\rho_\sigma(r) = \sum_{i=1}^{N_\sigma} |\varphi_{i,\sigma}(r)|^2 = \sum_{i=1}^{N_\sigma} \rho_{i,\sigma}(r) \qquad \sigma = \alpha, \beta \tag{6}$$

Which follow the normalization conditions

$$N_\sigma = \int dr\, \rho_\sigma(r) \qquad \sigma = \alpha, \beta \tag{7}$$

Electron number, N, and spin number N_s, are defined as

$$N = N_\alpha + N_\beta \quad \text{and} \quad N_S = N_\alpha - N_\beta \tag{8}$$

In this representation the spin potential, μ_S and a kind of chemical potential, μ_N, are given by (Galván et al., 1988; Galván and Vargas, 1992; Vargas et al., 2002)

$$\mu_N = \left(\frac{\partial E}{\partial N}\right)_{N_S, v(r)} \quad \text{and} \quad \mu_S = \left(\frac{\partial E}{\partial N_S}\right)_{N, v(r)} \tag{9}$$

The corresponding hardness parameters are

$$\eta_{NN} = \left(\frac{\partial \mu_N}{\partial N}\right)_{N_S, v(r)} \tag{10a}$$

$$\eta_{NS} = \left(\frac{\partial \mu_N}{\partial N_S}\right)_{N, v(r)} = \left(\frac{\partial \mu_S}{\partial N}\right)_{N_S, v(r)} = \eta_{SN} \tag{10b}$$

and

$$\eta_{SS} = \left(\frac{\partial \mu_S}{\partial N}\right)_{N, v(r)} \tag{10c}$$

3   COMPUTATIONAL DETAILS

Density functional theory (DFT) as implemented in Gaussian 03 (Gaussian 03, 2003) was used for all the calculations. We employed the functional B3PW91, which uses a combination of B3 (Becke, 1993) exchange functional and PW91 (Perdew et al., 1992) correlation functional. The LANL2DZ pseudopotential and the corresponding double- ζ basis set were used for silver and platinum atoms (Wadt and Hay, 1985).

The initial geometry of Ag_{10} cluster corresponds to an fcc arrangement in the bulk, Figure 1, and the binary structures was obtained by means of successive replacement of platinum atoms by silver atoms.The conformational space of the each binary systems was scanned using the molecular dynamics module of the HyperChem package (HyperChem, 1996).
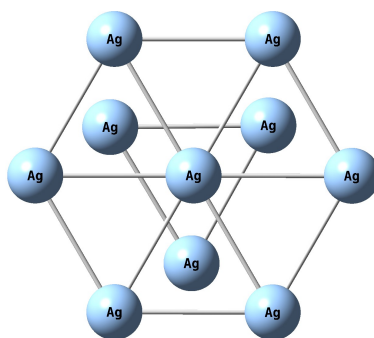
Figure 1: Top view of Ag$_{10}$ cluster in their initial configuration.

A full geometry optimization has been performed for all structures and vibrational analysis (without imaginary frequency) in order to be sure that structures obtained corresponds to stable clusters. Optimization were done checking different multiplicities (m), singlet (m=1) and triplet (m=3) states have been worked out for those clusters having even number of electrons and doublet(m=2) and quartet (m=4) states have been worked out for those having odd number of electrons. The structures with the lowest energy were chosen as the more stable configurations.

The stability of these clusters can be discussed on the basis of the binding energy per atom (E/a), defined as follows,

$$E/a = = \frac{E(Ag_m Pt_n) - mE(Ag) - nE(Pt)}{N} \tag{11}$$

where $m = 10 - x$ is the number of silver atoms, $n = x$ is the number of platinum atoms, N=m +n is the total number atoms and E(Ag$_m$Pt$_n$), E(Ag), E(Pt) are the total energies of Ag$_m$Pt$_n$ cluster and an isolated Ag and Pt atoms, respectively.

The global reactivity index, chemical potential and hardness, were obtained through Eqs. (1) y (2), respectively, using ionization potentials and electron affinities. Indeed, we have calculated the energy of cations and anions at the geometry of the neutral systems to determine the vertical IP = [E(N-1)-E(N)] and EA = [E(N)-E(N+1)] values. On the other hand, we have used operational formulas based on the well-known finite difference and frozen core approximations (Galván et al., 1988; Galván and Vargas, 1992; Vargas et al., 2002; Garcia et al., 1996) for the chemical-potential and hardness quantities entering into the definitions of Eqs. 9 and 10,

$$\mu^-_N = \frac{1}{2}\left(\varepsilon_{H\alpha} + \varepsilon_{H\beta}\right) \quad \mu^+_N = \frac{1}{2}\left(\varepsilon_{L\alpha} + \varepsilon_{L\beta}\right) \quad \eta_{NN} = \frac{\left(\mu^+_N - \mu^-_N\right)}{2} \tag{12}$$

and

$$\mu^-_S = \frac{1}{2}\left(\varepsilon_{H\alpha} - \varepsilon_{L\beta}\right) \quad \mu^+_S = \frac{1}{2}\left(\varepsilon_{L\alpha} - \varepsilon_{H\beta}\right) \quad \eta_{SS} = \frac{\left(\mu^-_S - \mu^+_S\right)}{2} \tag{13}$$

where the $\varepsilon_{i,\alpha,\beta}$ stands for the ith frontier eigenvalue of a given α or β spin state. Note from Eq. 13 that for an open-shell system, the chemical potential μ_N is positioned between the eigenvalues defining the minimum gap, and η_{NN} stands for the gap between the two constrained chemical potentials μ^-_N and μ^+_N. Note also that for a closed-shell system, i.e.,

$\varepsilon_{H\alpha} = \varepsilon_{H\beta} = \varepsilon_H$ and $\varepsilon_{L\alpha} = \varepsilon_{L\beta} = \varepsilon_L$, we have that $\mu_N = \mu$, and $\eta_{NN} = \eta$. On the other hand, from Eq. 13, the spin potentials $\mu_S^{\pm}$ constitute, in fact, the lowest unoccupied molecular orbital-highest occupied molecular orbital (LUMO-HOMO) gaps among the two spin symmetries (i.e., spin polarization).

4   RESULTS

The lowest-energy structures, symmetry group and multiplicity of Ag_xPt_{10-x} ($1 \leq x \leq 10$) series are showed in Figure 2. The ground state geometry of Ag_{10} is distorted square bypiramid with symmetry group C1, which has already been reported in the literature (Tian et al., 2007).
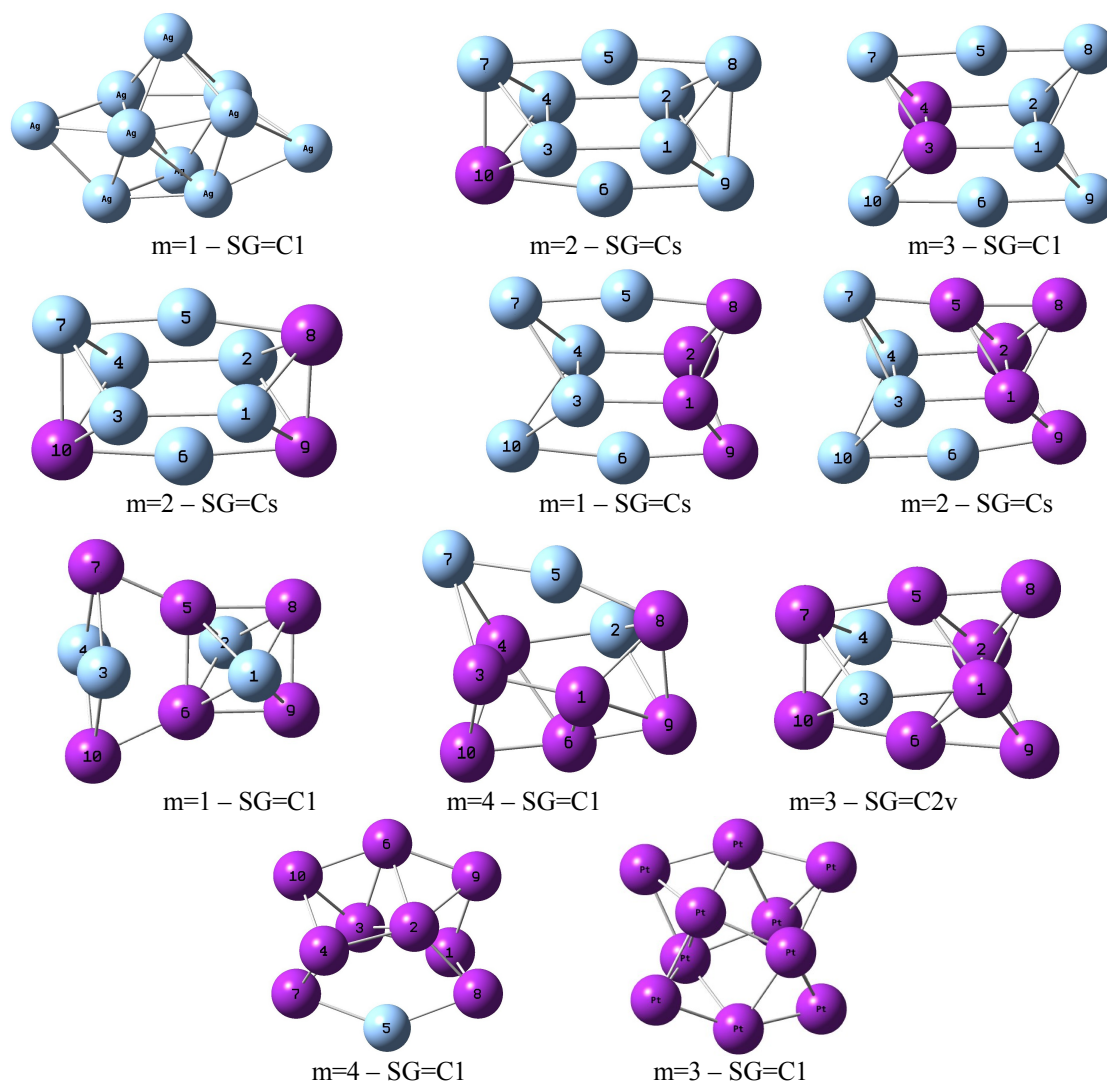

Figure 2: The equilibrium geometric structures, multiplicity (m) and symmetry group (SG) of Ag_xPt_{10-x} ($1 \leq x \leq 10$) series.

The addition of platinum atoms generated a geometric distortion and atomic reorganization in the original structure until the lowest energy structure of Ag_1Pt_9 whose structure is similar to ground-state geometry of Ag_{10}.

It is instructive to examine the change of average distances as a function of number of platinum, which is shown in Figure 3. There was hardly any variation in Ag-Pt distance, while Pt-Pt distance decreased continuously. For n=8 the Ag-Ag distance suddenly jumps to 4.13 A,

indicating that the formation of Pt-Pt bonds become more favorable keeping positively charged Ag ions far apart as a result of a significant charge transfer from Ag to Pt. The effect of competing interactions is thus clearly seen in the geometry changes.
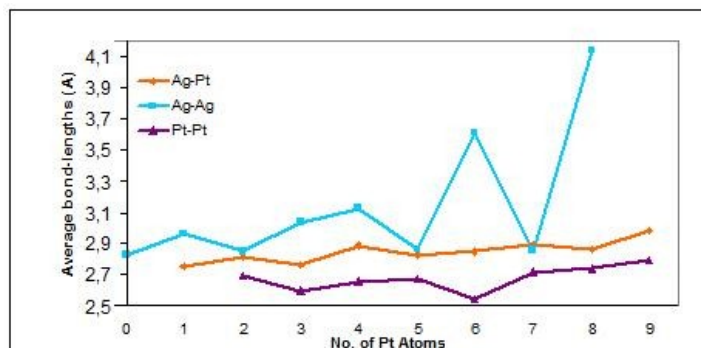

Figure 3: Average distances as a function of number of platinum

The binding energy per atom (E/a) as a function of number of Pt atoms is represented in Figure 4. As expected, the binding energy per atom increase (in absolute value) with increasing Pt content in the cluster. It is well known that the magnitude of E/a gives information about the strength of chemical bonds in clusters, thus increasing it indicates greater system stability.
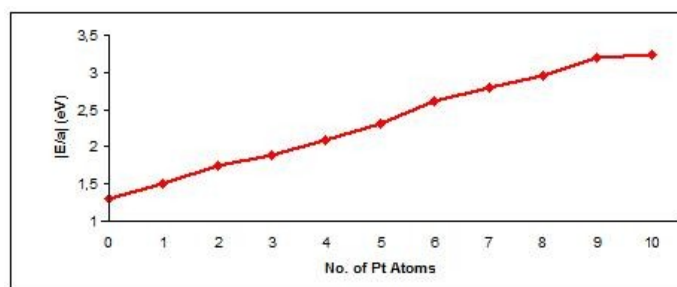

Figure 4: Binding energy per atom (E/a) as a function of number of Pt atoms

Table 1 shows the global reactivity indicators, chemical potential (μ) and chemical hardness (η), is observed that the highest chemical potential and lowest chemical hardness corresponds to Ag_6Pt_4 structure, therefore this system is the most reactive of the series.

system	μ_N (eV)	η_{NN} (eV)
Ag_{10}	-3,6263	2,1940
Ag_9Pt_1	-4,1690	2,1160
Ag_8Pt_2	-4,3562	2,2592
Ag_7Pt_3	-4,3000	1,7910
Ag_6Pt_4	-4,0908	1,7515
Ag_5Pt_5	-4,2306	1,7623
Ag_4Pt_6	-4,4899	2,0634
Ag_3Pt_7	-4,6225	1,9092
Ag_2Pt_8	-4,8270	1,7994
Ag_1Pt_9	-4,9525	1,9750
Pt_{10}	-5,2397	1,9605

Table 1: Global reactivity indicators: chemical potential and chemical hardness in eV.

5 CONCLUSIONS

In this work we performed a systematic study for the structure, energetics and reactivity of Ag_xPt_{10-x} nanoalloys. The calculations were carried out using the spin-polarized density functional theory formalism. Based on the results we concluded that:

- Changing the concentration of nanoalloy AgPt by the substitution of silver atoms by platinum atoms stabilized the structures and produced a geometric distortion and atomic reorganization product of the charge transfer process.

- The analysis of indicators of reactivity appeared to be very effective at identifying the most reactive structures, being the most reactive Ag_6Pt_4 structure of the series under study.

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