

Aluminium-Silicon nanoalloys: structures and stabilities

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Abstract: Clusters have been a central theme in the development of nanotechnology research, and its study allows the development of properties tunable by size in the nanometric scale.^[1] Agglomerates consisting of two or more metal elements are called nanoalloys, and may also be tuned by composition. These are highly reactive, and can be prepared by means of beam techniques or by matrix isolation.^[1] The metallic nanoalloys that are the object of this work, have as components aluminum and silicon. Al clusters have been extensively studied, both experimentally and theoretically, due to their wide application in the field of catalysis, electronics, among others.^[1,2] Si clusters are of great interest because of two potential applications in the semiconductor and optoelectronic industries. The Al-Si compounds have considerable significance in the nanomaterials areas.^[3] To investigate these alloys theoretically it is necessary first to determine the geometrical configuration of the most stable structures, which is difficult due to the large number of isomers generated by the permutations of Al and Si atoms (called homotops).^[4] The objective of this work is to predict the stability of such clusters, employing previously determined geometries. For this purpose, clusters between three and thirteen atoms with the lowest energies are considered. The structures were optimized using the Möller-Plesset Perturbation Theory (MP). A basis set was used that has an effective core potential (ECP), where the innermost electrons are disregarded (LANL2DZ), culminating in a faster calculation.^[5,6] The results are refined using CCSD and compared to DFT calculations with larger basis sets. The software used for the calculations was the General Atomic and Molecular Electronic Structure System (GAMESS), version 2016^[7] and for visualization wxMacMolPlt was used.^[8] The results obtained are interpreted according to the reactivity and stability of the structures using binding energy, excess energies and the HOMO-LUMO gap. The binding energy (eq.1) gives us the stability of the clusters as a function of composition.^[4]

$$E_b(Al_xSi_y) = E(Al_xSi_y) - xE(Al) - yE(Si) \quad \text{eq.1}$$

According to the binding energy analysis, the larger the amount of silicon atoms in the cluster composition, the more likely they are to become more stable. By means of the excess energy (eq.2), the favorability of the formation of alloy rather than the corresponding pure clusters can be obtained.^[4] A negative value indicates that the formation of the corresponding nanoalloy is favored.

$$E_{exc}(Al_xSi_y) = E_b(Al_xSi_y) - x \frac{E_b(Al_N)}{N} - y \frac{E_b(Si_N)}{N} \quad \text{eq.2}$$

The excess energy analysis indicates that smaller clusters tend to be more stable in the homonuclear form, whereas in cluster with 8, 9 and 11 atoms mixing is favored.



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HOMO-LUMO gaps, electron affinity and ionization energies are also relevant to estimate the reactivity of the clusters and will also be calculated.

Key-words: cluster, nanoalloy, Al-Si, bonding energy, excess energy.

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