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Supporting Information for: Segregation Effects on the Properties of $(AuAg)_{147}$

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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3.2 Chemical Ordering for Au_nAg_{147-n} Nanoalloys

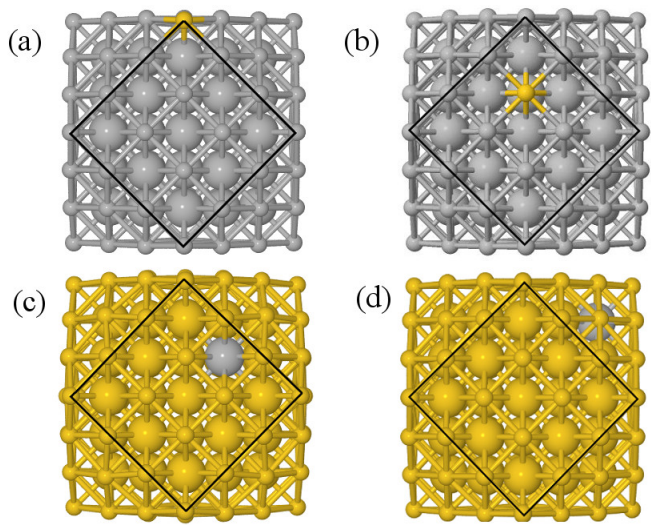

Fig. 1. Lowest energy arrangements for atomically doped structures: (a) $E_{min}^{DFT}(Au_1Ag_{146})$; (b)$E_{min-1}^{DFT}(Au_1Ag_{146})$; (c) $E_{min}^{DFT}(Au_{146}Ag_1)$; (d)$E_{min-1}^{DFT}(Au_{146}Ag_1)$. The outer geometric shell, or surface layer, is represented as ball−and−stick to emphasize the positioning of the dopant atom, with the atomic radius of the sub-surface atoms increased to highlight their depth. Both (a) and (b) have Au in a surface position, whilst (c) and (d) show Ag subsurface. Au and Ag atoms are represented by yellow and grey spheres, respectively.

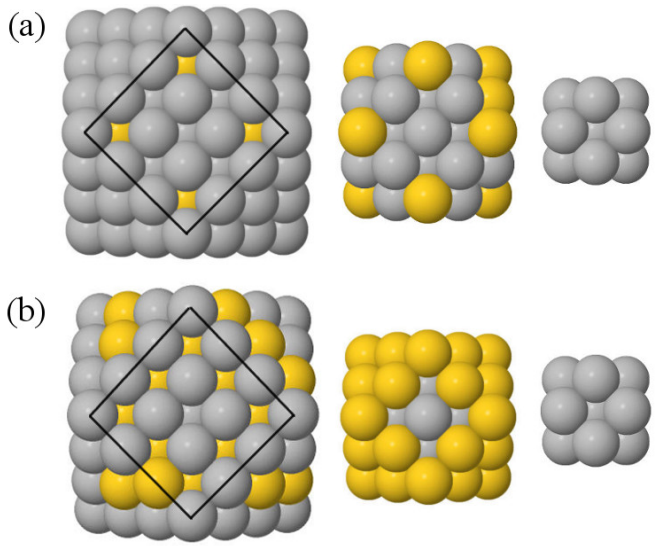

Fig. 2. Same structures as in Fig. 5. (a) and (b), removing the outermost subshell as one moves left to right: 147 atoms; 55 atoms; and 13 atoms for (a) $Au_{13}Ag_{134}$ and (b) $Au_{55}Ag_{92}$. The propensity of Au to occupy sub−vertex positions illustrates the tendency towards the formation of Ag@Au@Ag.

Table I. Change in E_b and E_{exc} for all systems (lowest energy alloy arrangements) investigated (ΔE_{exc} and ΔE_b, respectively) with values given relative to the structure with the lowest ΔE_{exc} or ΔE_b. [All cases given relative to the lowest value]. The Fermi Energy (E_F) is given in the final column. All values are given in eV.

Structure	ΔE_b^{Gupta}	ΔE_{exc}^{Gupta}	ΔE_b^{DFT}	ΔE_{exc}^{DFT}	E_F
Ag_{147}	0.000	12.959	0.000	4.499	−3.996
Au_1Ag_{146}	0.008	12.549	0.004	4.384	−4.013
$Au_{13}Ag_{134}$	0.108	7.864	0.052	3.204	−4.067
$Au_{13}@Ag_{134}$	0.082	11.738	0.051	3.364	−3.964
$Au_{55}Ag_{92}$	0.388	1.150	0.200	2.080	−4.227
$Au_{55}@Ag_{92}$	0.372	3.420	0.184	4.470	−4.039
$Au_{74}Ag_{73}$	0.500	0.135	0.263	2.212	−4.335
$Au_{92}Ag_{55}$	0.602	0.000	0.319	2.746	−4.515
$Ag_{55}@Au_{92}$	0.551	7.379	0.338	0.000	−4.802
$Au_{134}Ag_{13}$	0.818	2.561	0.437	6.040	−4.808
$Ag_{13}@Au_{134}$	0.815	2.971	0.436	6.296	−4.873
$Au_{146}Ag_1$	0.873	4.190	0.466	7.789	−4.839
Au_{147}	0.879	4.336	0.468	7.956	−4.830

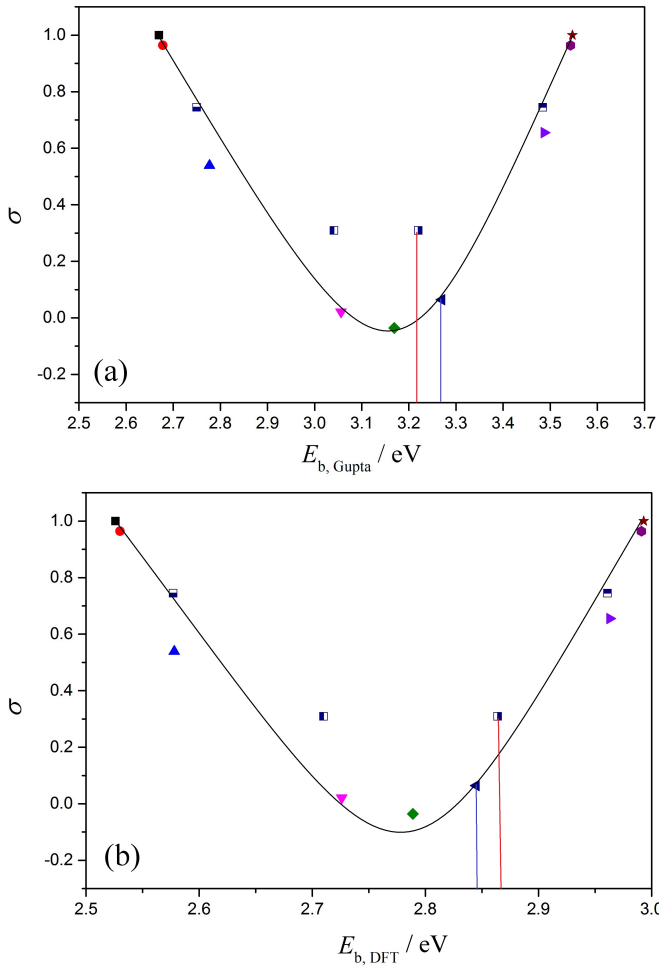

Fig. 3. (a) E_b^{Gupta} and (b) E_b^{DFT} against the extent of mixing within the nanocluster, σ. The line is only given as a guide to the eye; symbols are the same as in Fig. 5 of the main text. The red and blue lines are to emphasize the difference in E_b^{Gupta} and E_b^{DFT} between the alloy and its corresponding core@shell arrangement.

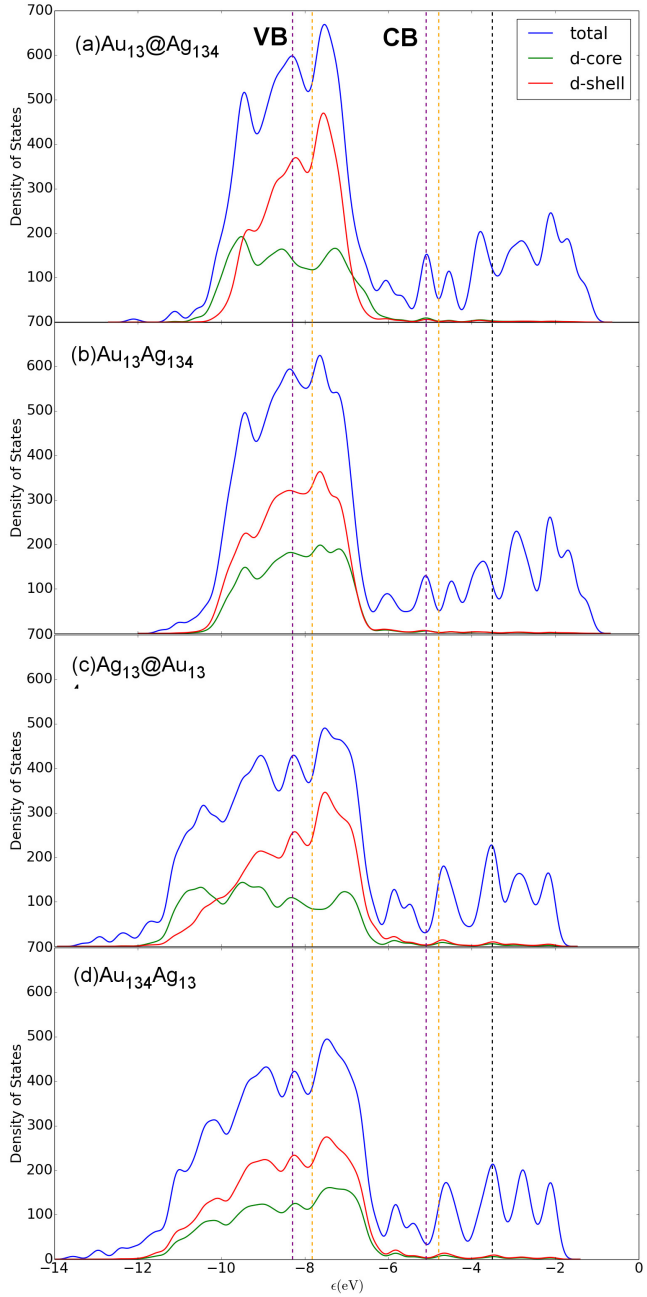

Fig. 4. DOS profiles for both alloys and core@shell compositions: (a) Au_{13}@Ag_{134}, (b) $Au_{13}Ag_{134}$, (c) Ag_{13}@Au_{134}, (d) $Au_{134}Ag_{13}$. A key is provided. E_F is given as a black dotted line, with the valence band maximum (VBM) and conduction band minimum (CBM), in purple and orange, for anatase and rutile TiO_2, respectively. A Gaussian broadening of 0.05 eV has been used for the electronic states.

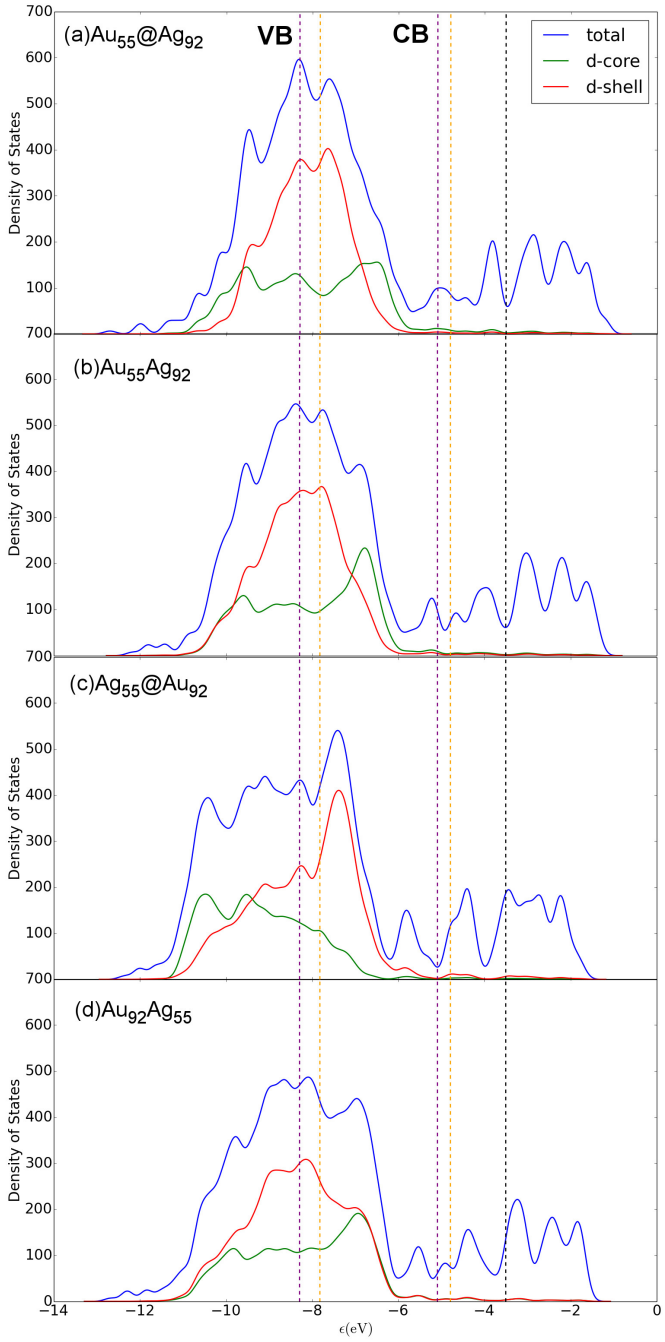

Fig. 5. DOS profiles for both alloys and core@shell compositions: (a) Au_{55}@Ag_{92}, (b) $Au_{55}Ag_{92}$, (c) Ag_{55}@Au_{92}, (d) $Au_{92}Ag_{55}$. A key is provided. E_F is given as a black dotted line, with the valence band maximum (VBM) and conduction band minimum (CBM), in purple and orange, for anatase and rutile TiO_2, respectively. A Gaussian broadening of 0.05 eV has been used for the electronic states.