- Supporting Information -

for

Interaction in Multilayer Clusters: A Theoretical Survey of $[Sn@Cu_{12}@Sn_{20}]^{12-}$, a Three-layer Matryoshka-like Intermetalloid.

Markus Rauhalahti[b], Alvaro Muñoz-Castro[a]

[a]*Direccion de Postgrado e Investigación, Sede Providencia, Universidad Autonoma de Chile, Llano Subercaceaux 2801, San Miguel, Santiago, Chile.*

[b]*Department of Chemistry, University of Helsinki, P.O. Box 55 (A. I. Virtanens plats 1), FIN-00014 University of Helsinki, Finland*

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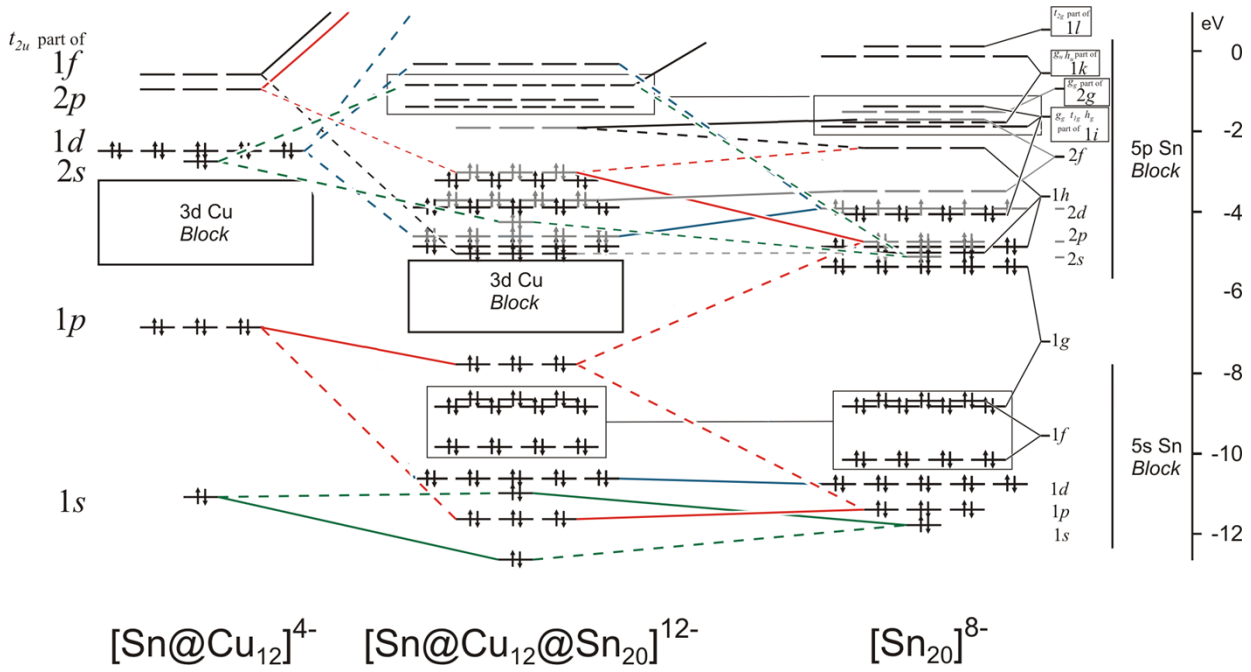

Figure S1. Electronic structure of $[Sn@Cu_{12}@Sn_{20}]^{12-}$ denoting the contribution from the 20-*ve* core $[Sn@Cu_{12}]^{4-}$ and the $[Sn_{20}]^{8-}$ outer-shell. Color lines denotes *s*- (green), *p*- (red), *d*- (blue), and other types of interaction (black). The second set of superatomic levels of $[Sn_{20}]^{8-}$ is denoted in gray.

Table S1. Spanning of the combination of atomic functions involved in the formation of $[E@M_{12}@E_{20}]^{q-}$, into the *Ih* point group.

	M_{12}	E_{20}
ns	$a_g \oplus t_{1u} \oplus t_{2u} \oplus h_g$	$a_g \oplus t_{1u} \oplus t_{2u} \oplus g_g \oplus g_u \oplus h_g$
np	$a_g \oplus t_{1g} \oplus 2\ t_{1u} \oplus t_{2u} \oplus 2g_g \oplus 2h_g \oplus h_u$	$a_g \oplus t_{1g} \oplus t_{2g} \oplus 2t_{1u} \oplus 2t_{2u} \oplus 2g_g \oplus 2g_u \oplus 3h_g \oplus 2h_u$
np_{radial}	$a_g \oplus t_{1u} \oplus h_g \oplus t_{2u}$	$a_g \oplus t_{1u} \oplus h_g \oplus g_u \oplus t_{2u} \oplus g_g$

Table S2. Compatibility table between the full rotational group and the *Ih* point group.

l=		Γ^{Ih}
0	*s*	a_g
1	*p*	t_{1u}
2	*d*	h_g
3	*f*	$g_u \oplus t_{2u}$
4	*g*	$g_g \oplus h_g$
5	*h*	$h_u \oplus t_{1u} \oplus t_{2u}$
6	*i*	$a_g \oplus t_{1g} \oplus g_g \oplus h_g$
7	*k*	$t_{1u} \oplus t_{2u} \oplus g_u \oplus h_u$
8	*l*	$t_{2g} \oplus g_g \oplus 2h_g$

Inclusion of the Spin-Orbit coupling

In addition, we briefly discuss the inclusion of the spin-orbit term [1] into the description of the electronic structure of a super-atom under the jellium framework, as has been considered recently [2]. The splitting of the levels with $l \neq 0$ in the $[Sn@Cu_{12}]^{4-}$ into the *j-j* coupling scheme leads to $1p \rightarrow 1p_{1/2} \oplus 1p_{3/2}$ with a spin-orbit constant (ξ_{SO}) of 1048.9 cm^{-1} denoting the energy gap between those eigenvalues according to the *total angular momentum* representation, the shell with $l=2$ split as, $1d \rightarrow 1d_{3/2} \oplus 1d_{5/2}$ with ξ_{SO} = 100,7 cm^{-1}, and the $2p$ jellium level split as, $2p \rightarrow 2p_{1/2} \oplus 2p_{3/2}$ with a ξ_{SO} = 782,2 cm^{-1}. According to this, the *inner-core* $[Sn@Cu_{12}]^{4-}$ and $[As@Ni_{12}]^{3-}$ which displays a $1s^2 1p^6 2s^2 1d^{10}$ and $1s^2 1p^6 2s^2$ jellium level sequence, due to the spin-orbit coupling are denoted as: $1s_{1/2}^2 1p_{1/2}^2 1p_{3/2}^4 2s_{1/2}^2 1d_{3/2}^{10} 1d_{5/2}^{10}$ and $1s_{1/2}^2 1p_{1/2}^6 1p_{3/2}^6 2s_{1/2}^2$.

Into the overall $[Sn@Cu_{12}@Sn_{20}]^{12-}$ cluster, the resulting levels involving such levels split as follows, $1p \rightarrow 1p_{3/2} \oplus 1p_{1/2}$ ξ_{SO} = 256,1 cm^{-1}; $1d \rightarrow 1d_{3/2} \oplus 1d_{5/2}$ ξ_{SO} = 270,0 cm^{-1}; $2p \rightarrow 2p_{1/2} \oplus 2p_{3/2}$ ξ_{SO} = 963,0 cm^{-1}; $2d \rightarrow 2d_{5/2} \oplus 2d_{3/2}$ ξ_{SO} = 921,0 cm^{-1} and $3p \rightarrow 3p_{3/2} \oplus 3p_{1/2}$ ξ_{SO} = 323,5 cm^{-1}.

References

[1] **(**a) Dyall, K. G. and Fægri, K. Introduction to Relativistic Quantum Chemistry, Oxford University Press, New York, 2007. (b) Grant, I. P. Relativistic Quantum Theory of Atoms and Molecules, Theory and Computation, Springer, New York, 2007.

[2] (a) Muñoz-Castro, A. Golden Endohedral Main-Group Clusters, $[E@Au_{12}]^{q-}$: Theoretical Insights Into the 20-e Principle, *J. Phys. Chem. Lett*, **2013**, 4, 3363-3366. (b) Muñoz-Castro, A.; Arratia-Perez, R. Spin-Orbit Effects on a Gold-Based Superatom: A Relativistic Jellium Model. *Phys. Chem. Chem. Phys*. **2012**, 14, 1408-1411. (c) Muñoz-Castro, A.; D. Mac-Leod Carey, D.; Arratia-Perez, R. Inside a Superatom: The M_7^q (M=Cu, Ag, q=1+, 0, 1-) Case. *ChemPhysChem* **2010**, 11, 646-650.

Credits for the icosahedron and dodecahedron model displaying the geophisical data of the Globe used in the Table of Contents image.

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http://www.ngdc.noaa.gov/mgg/image/dodecahedron.pdf