Supporting Information for

Comment on "Uncommon structural and bonding properties in $Ag_{16}B_4O_{10}$" by A. Kovalevskiy, C. Yin, J. Nuss, U. Wedig, and M. Jansen, Chem. Sci., 2020, 11, 962

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Computational details

The size of the active valence space (core only, outer-core, pseudopotentials, etc.) and the number of *k*-points in the reciprocal Brillouin zone have an impact in the selection of the procedures to search critical points and may affect quantitatively specific ELF values. It is convenient to bear also in mind that the goal of this comment is to discuss the chemical bonding network with explicit focus on the silver valence electrons. Based on our previous experience with the ELF topological analysis in crystalline solids (see for example Refs. 1 and 2), we have selected a balanced option, in terms of computational cost and accuracy, including 3, 6, and 11 valence electrons for B, O, and Ag, respectively, along with 4x4x6 ($Ag_{16}B_4O_{10}$) and 12x12x12 (*fcc*-Ag) k-point grids. Real space grids of 200x200x128 ($Ag_{16}B_4O_{10}$ and $Ag_{16}\square_4$) and 64x64x64 (*fcc*-Ag) data points were used for both the ELF and the electron density. Although in Ref. 3 a different code and enhanced computational parameters were used, only slight quantitative differences might be expected when results from both approaches are compared.

Results

fcc pure silver metal

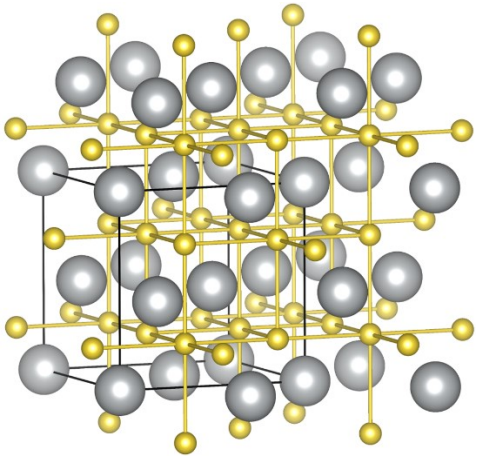

Figure S1. 3D-circuit (yellow lines) connecting ELF valence attractors (yellow balls) in pure *fcc* silver metal. Grey balls denote Ag atoms.

Defective silver-vacant structure

Table S1. Basin electron population (Basin Pop) and distance to the vacancy center (d_{void}) in Å of ELF attractors in the defective silver-vacant lattice. Mult. and NN stand for the multiplicity and number of nearest vancancy centers to the attractor, respectively. ID colors identify the different attractors as depicted in Fig. 3 of the manuscript.

ID color	Basin Pop	d_{void}	Mult.	NN
Black	0.501	3.70	16	4
Orange	0.498	4.31	4	8
Cyan	0.400	4.85	16	8
Green	0.373	4.80	16	4
Pink	0.302	4.72	16	4

The shorter the distance of the attractors to the vacancy center and the greater the number of nearest vacancies, the larger is the electron population of the basin associated with the attractor. This behaviour is due to an effective decrease in the number of delocalized electrons in the *fcc*-lattice induced by the Ag_4 vacancy in its surroundings. As a consequence, Ag atoms conforming attractors

close to and more surrounded by the vancancy centers (black, orange and cyan) should display greater valence oxidation states on average than those associated with pink and green attractors.

Silver borate structure

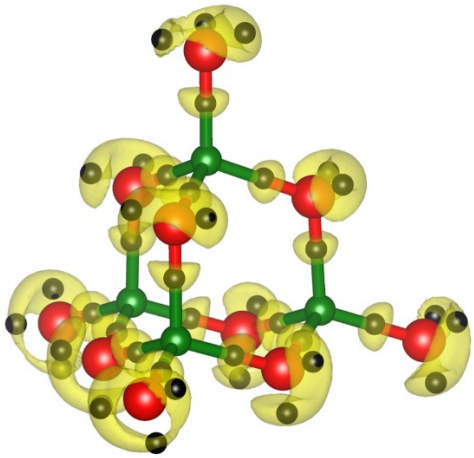

Figure S2. ELF yellow isosurface (η = 0.82) of the B_4O_{10} cluster. Attractors are denoted with small black balls. Red and green balls stand for oxygen and boron atoms, respectively.

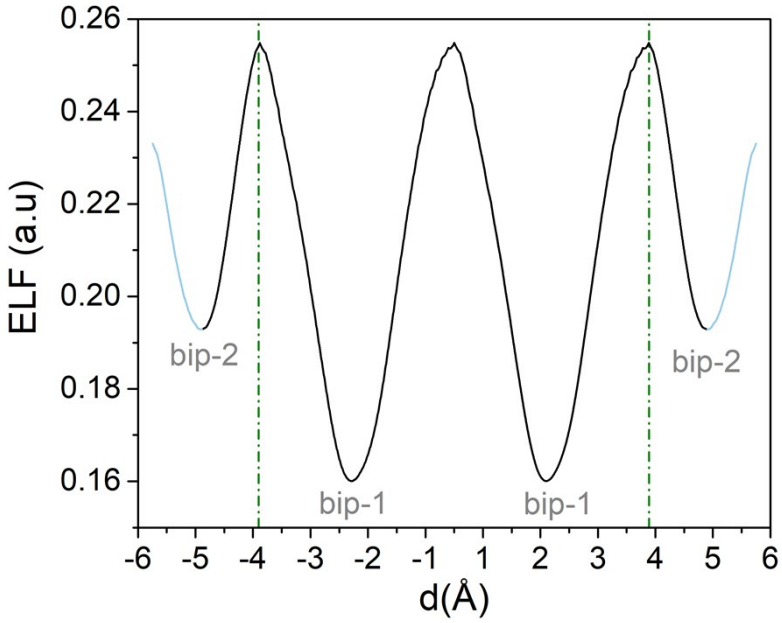

Figure S3. ELF one dimensional profile connecting cyan-black-black-black-cyan attractors in $Ag_{16}B_4O_{10}$. Cyan-black and black-black bonding interaction points are labelled as bip-1 and bip-2, respectively.

1 J. Contreras-García, A. M. Pendás, J. M. Recio and B. Silvi, *J. Chem. Theory Comput.*, 2009, **5**, 164–173.

2 J. Contreras-García, P. Mori-Sánchez, B. Silvi and J. M. Recio, *J.Chem. Theory Comput.*, 2009, **5**, 2108-2114.

3 A.Kovalevskiy, C. Yin, J. Nuss, U. Wedig and M. Jansen, *Chem. Sci.*, 2020, **11**, 962–969.