# Density functional analysis of the electronic structure of $Cs_9InO_4$:

# Evidence for the presence of a $Cs^-$ anion

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Compounds of the type $Cs_9MO_4$ (M = In, Fe, Sc..) [1] are excellent electric conductors, their resistivity approaching that of metallic cesium. The complex oxoindate $Cs_9InO_4$ can be described in terms of an ion/electron counting scheme $(Cs^+)_9[(In^{3+})(O^{2-})_4]+4e^-$. The surplus of electrons is associated with the cesium atoms, so the structure can be divided into an ionic part with localized electrons in the oxoindate anion and a metallic part with delocalized electrons in the cesium sublattice, see Figure 1a). However, the cesium atoms in $Cs_9InO_4$ exhibit quite different environments so that the valence electron distribution within the metallic part of the structure is expected to be highly non-uniform. In $Cs_9InO_4$ the shortest Cs–O distances involving the Cs(1), Cs(2) and Cs(3) atoms (i.e. 281, 292 and 312 pm, respectively) are similar to those in the structure of salt-like $Cs_2O$ (i.e. 292 pm), indicating that these Cs atoms behave as $Cs^+$ ions towards oxygen. In contrast, the Cs(4) atom is located at the center of a $Cs_{16}$ cage made up of eight Cs(1), four Cs(2), four Cs(3) and two additional Cs(4) atoms from an adjacent cage (Figure 1b) with Cs–Cs distances ranging from 531 to 645 pm, similar to what is found for elemental bcc cesium. This analysis of the Cs–Cs distances corroborates our view of the metal-metal bonding between the cesium atoms resulting in a delocalized electronic system and the ionic bonding to the $InO_4$ entities according to $(Cs^+)_9[InO_4^{5-}]+4e^-$. However, the excess cannot be uniformly distributed among the cesium atoms because they have very different environments.
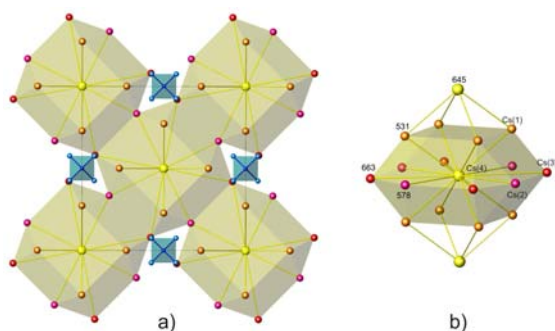


Figure 1: (a) Projection of the tetragonal crystal structure of $Cs_9InO_4$ along [001]. The $InO_4$ tetrahedra are given in blue, and the Cs sublattice in yellow. (b) Perspective view of the coordination polyhedron around Cs(4) in $Cs_9InO_4$ together with Cs-Cs distances [pm].

In order to analyze the chemical bonding in more detail we have performed density functional theory electronic structure calculations for $Cs_9InO_4$. [2] The narrow band in the total density of states (DOS) (Figure 2 a) around -14 eV signifies the O 2s states followed by the 5p states of cesium at around -10 eV with essentially no contribution from indium and oxygen. The bands in the energy range from -6 to -2 eV originate from the $InO_4^{5-}$ anion (mainly O 2p mixed with In 5s states) as indicated by the MO scheme based on Extended Hückel calculations for the highest occupied states of a discrete $InO_4^{5-}$ entity, which shows the splitting of the 12 O 2p orbitals of the 4 O atoms, see inset of Figure 2a).
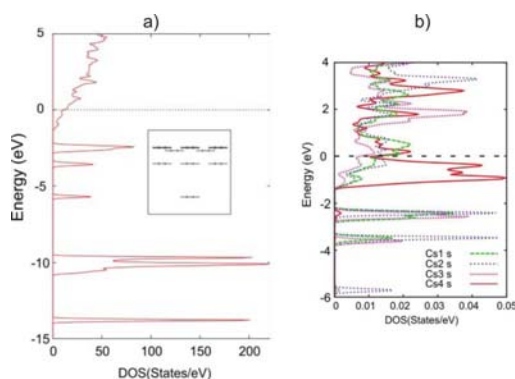


Figure 2: (a) Total DOS of $Cs_9InO_4$ together with the MO scheme for the highest occupied states of a discrete $InO_4^{5-}$ tetrahedron as inset. (b) Partial DOS plots for the different Cs atoms in $Cs_9InO_4$.

The band gap around $-2eV$ separates the states with contributions from the $InO_4$ tetrahedra from the states with contributions of the Cs atoms, see the partial DOS (PDOS) plots calculated for the Cs 6s orbitals of the Cs(1) to Cs(4) atoms in $Cs_9InO_4$ shown in Figure 2b). A filling of these bands from this band gap up to the Fermi level corresponds to the 4 extra electrons in $Cs_9InO_4$. The 6s contributions of Cs(1), Cs(2) and Cs(3) lie well below the Fermi level where the O 2p states occur because of their Cs-O interactions. For Cs(4), a significant 6s density of states accumulates below the Fermi level.

To gain more insight into the bonding between the Cs atoms in the $Cs(4)Cs_{16}$ cluster of $Cs_9InO_4$, we have calculated the crystal orbital Hamilton population (COHP) using the LMTO code. The COHP curves indicate that there are significant bonding interactions below the Fermi level among the Cs(1), Cs(2) and Cs(3) atoms that form the $Cs_{16}$ cage surrounding each Cs(4) atom (see Figure 3a). The associated Cs–Cs distances range from 387 to 490 pm. In contrast, the interactions of the Cs(4) atom with the surrounding Cs(1), Cs(2) and Cs(3) atoms are approximately ten times weaker, in agreement with the much larger Cs–Cs distances of 531 to 673 pm (see Figure 3b). Below the Fermi level, the COHP is positive for Cs(4)–Cs(1) but negative for Cs(4)–Cs(2) and Cs(4)–Cs(3). Given the lower-lying 6s level of Cs(4) and the higher-lying 6s levels of $Cs(1)^+$, $Cs(2)^+$ and $Cs(3)^+$, one might have expected positive COHP for all the Cs(4)–Cs(1), Cs(4)–Cs(2) and Cs(4)–Cs(3) interactions. The negative COHP for Cs(4)–Cs(2) and Cs(4)–Cs(3) with long Cs–Cs distances (578 and 663 pm, respectively) is due most likely to the counterintuitive orbital interactions of the doubly-filled 6s orbital of Cs(4) with the empty 6s orbitals of $Cs(2)^+$ and $Cs(3)^+$. This point is corroborated by the calculation of the electron localization function (ELF) (see below). Thus, the analysis of the COHP curves is consistent with the assignment of an anionic $Cs(4)^-$.
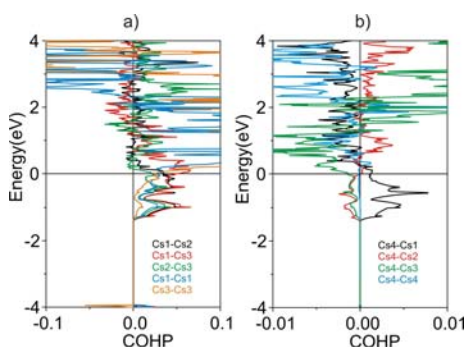


Figure 3: COHP curves for a) the Cs-Cs interactions between the Cs atoms forming a $Cs_{16}$ polyhedron around a Cs(4) atom in $Cs_9InO_4$ and b) for the interactions of the central Cs(4) atoms to the surrounding Cs(1), Cs(2), Cs(3) and Cs(4) atoms.

We have also analyzed the bonding feature of the $Cs(4)Cs_{16}$ cage of $Cs_9InO_4$ in terms of the electron localization function (ELF) based on LMTO band structure calculations. Figure 4 shows a cross-section view of the ELF around a $Cs(4)Cs_{16}$ polyhedron in the (002) plane containing the Cs(4), Cs(2) and Cs(3) atoms. The presence of local maxima in the space between Cs(4) and Cs(2)/Cs(3) atoms indicates electron correlation minima and thus the presence of bonding between Cs(4) and the coordinating Cs(2) and Cs(3) atoms, and therefore supports our suggestion that the negative COHP for the Cs(4)-Cs(2) and Cs(4)-Cs(3) contacts actually represents bonding and arises from the counterintuitive orbital interactions. It is worth mentioning that no other unique attractors were found in the valence region at other positions within the $Cs(4)Cs_{16}$ polyhedra. The ELF analysis is again consistent with the description of $Cs_9InO_4$ as $(Cs(1)^+)_4(Cs(2)^+)_2(Cs(3)^+)_2Cs(4)^-[InO_4]^{5-}+2e^-$.
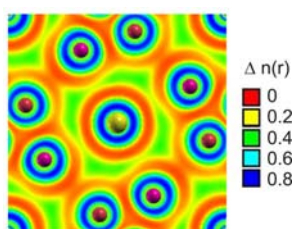


Figure 4: Distribution of ELF in the (002) plane calculated with the core states included containing the Cs(4), Cs(2) and Cs(3) atoms. The dark blue rings correspond to the penultimate shells of the Cs atoms. The occurrence of local maxima (i.e., the green regions) in the space between the Cs(4) and Cs(2)/Cs(3) atoms indicates multicenter bonds among these Cs atoms.

**References:**

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[2]  *C. Hoch, A. Simon, C. Lee, M.-H. Whangbo, J. Köhler.* Z. Kristallogr. **226**, 553 (2011)

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