

Electronic Structure Study of Gold Selenides

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The electronic structures of α - and β -gold selenides are studied. α - and β -AuSe are known as mixed valence compounds having linear (AuSe_2 , Au^+) and square-planar (AuSe_4 , Au^{3+}) units in their structure simultaneously. Our EHTB calculations, however, show that the oxidation states of Au in α - and β -AuSe are both close to +1. This is because the frontier orbitals are largely made up of Se p-orbitals and Au d-orbitals that lie well below the Fermi level. Our results are consistent with the recent X-ray absorption spectroscopy study on AuSe which show that all Au in the compound exhibit a monovalent state independent of their chemical environments.

Introduction

A mixed valence compound contains an element in two formally different oxidation states. The majority of such compounds involve transition metals, which can exist in a variety of oxidation states. Due to the interactions between the ions of differing oxidation states, the properties of mixed valence materials are often more varied than would be predicted on the basis of the properties of the individual ions involved. Many mixed valence compounds exhibit an intense absorption in the visible region, while compounds containing ions having only one of the constituent oxidation states are pale or colorless. An illustrative example is the Wolfram's red salt (WRS), $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$.¹ This compound consists of $\cdots\text{Pt}(\text{L})_4\cdots\text{Cl}-\text{Pt}(\text{L})_4\cdots\text{Cl}\cdots$ chains ($\text{L}=\text{C}_2\text{H}_5\text{NH}_2$), in which short and long platinum-chlorine distances ($\text{Pt}-\text{Cl}$ and $\text{Pt}\cdots\text{Cl}$) occur to give two structurally distinct platinum: one 6-coordinate Pt^{4+} (d^6 , $\text{Pt}(\text{L})_4\text{Cl}_2$) and the other roughly square-planar Pt^{2+} (d^8 , $\text{Pt}(\text{L})_4$). Neither $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4]^{2+}$ nor $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_2]^{2+}$ has an absorbance in the visible, while WRS has a deep red color due to an intervalence electron transfer, $\text{Pt}^{2+} \rightarrow \text{Pt}^{4+}$. Vibrational and photoelectron spectroscopy studies are in agreement with this proposed electron localization. As in the case of WRS, the ions in mixed valence compounds are frequently found to occur in two crystallographically distinguishable sites.

Gold halides are other known mixed valence compounds in which Au^+ and Au^{3+} coexists.² Typically, the trivalent gold is said to occupy a square coplanar AuX_4 group, and the univalent gold a linear AuX_2 site. An important issue inseparable from the discussion of formal oxidation states is the d-electron count scheme. For example, Au^+ , Au^{2+} , and Au^{3+} ions are often regarded as d^{10} , d^9 , and d^8 ions, respectively. The d-electron count scheme described above is based on a qualitative theory of electronic structure developed for those transition metal compounds whose frontier orbitals are largely made up of the metal d orbitals, *i.e.*, those systems in which the metal d orbitals lie higher in energy than do the ligand p orbitals. The Wells' cesium salt analogues $\text{Cs}_2\text{Au}_2\text{X}_6$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)³⁻⁶ are well-known mixed valence

gold compounds in which AuX_2 and AuX_4 units exist. Therefore, two different gold ions (*i.e.*, Au^+ and Au^{3+}) are expected in the compounds. However, recent electronic structure calculations on $\text{Cs}_2\text{Au}_2\text{X}_6$ ($\text{X}=\text{Cl}, \text{I}$) show that the oxidation state is +1 for Au in both AuX_2 and AuX_4 unit.⁷ This means that the metal d-orbitals are lower in energy than are the ligand p-orbitals, which is opposite to the expected d-electron count scheme.

α - and β -AuSe are non-halide gold compounds that have been believed to illustrate the mixed valency.⁸ As in the case of the Wells' cesium salt, they possess 2- and 4-coordinate gold ions. Both are jet black in color, as expected for mixed valence systems with shared ligands bridging the cations. The color was believed to arise from the small energy required for the electron transfer from the linear AuSe_2 unit to the square-planar AuSe_4 unit. Upon counting the formal charge of Se as -2, those of Au are expected to be +1 and +3 in linear and square-planar structure, respectively.⁸ However, as in the case of the Wells' cesium salt, it is necessary to investigate the limitation of the usual mixed-valence description and the associated d-electron count scheme in describing the electronic structures of compounds by examining whether the transition metal d-orbitals are higher in energy than are the ligand p-orbitals. We probe this question by performing extended Hückel tight-binding (EHTB)⁹ electronic band structure calculations for the α - and β -gold selenides. The atomic parameters employed for our EHTB calculations are listed in Table 1.

Structural Aspects

The syntheses and properties of α - and β -AuSe have been reported by Cranton *et al.*, and by Rabenau *et al.*¹⁰ Both are black in color, and they have the form of thin needles (α -AuSe) or of thin plates (β -AuSe). The crystal structures of these compounds have been determined thereafter.^{10b} X-ray diffraction data of these compounds suggest that the structures of both are closely related to the rock-salt type with one heavy metal atom being coordinated with four Se atoms and one being two Se atoms. However, the X-ray reflection calculated for these structures and the observed values suggest

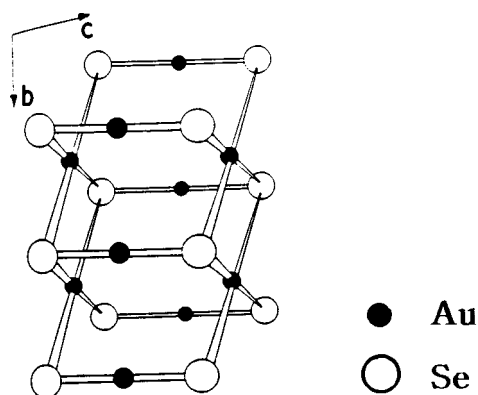
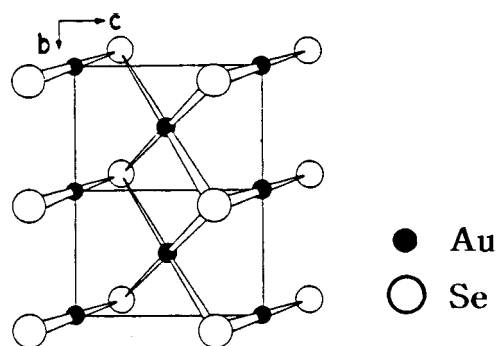
Table 1. Exponents ζ_i and Valence Shell Ionization Potentials H_{ii} of Slater Type Orbitals χ_i Used for Extended Hückel Tight-Binding Calculations

atom	χ_i	H_{ii}	ζ_i	c_{1i}^a	ζ_i	c_{2i}^a
Au	6s	-10.92	2.602			
Au	6p	-5.55	2.584			
Au	5d	-15.076	6.163	0.6851	2.794	0.5696
Te	5s	-20.8	2.51			
Te	5p	-13.2	2.16			
I	5s	-18.0	2.679			
I	5p	-12.7	2.322			
Se	4s	-20.5	2.44			
Se	4p	-13.2	2.07			
Br	4s	-22.07	2.588			
Br	4p	-13.1	2.131			
Cl	3s	-26.3	2.183			
Cl	3p	-14.2	1.733			

^aCoefficient in double- ζ expansion of 3d function.

that these compounds show a distortion of the ideal rock-salt. The structure distortion is possibly due to the grouping of the selenium atoms closer to the 4-coordinated Au atoms than to the linearly coordinated Au.

As mentioned earlier, two different Au are present in α -AuSe: One is linearly coordinated to two Se atoms (hereafter we denote atoms in this unit as Au-2) while another has a square-planar coordination formed by four Se atoms (hereafter we denote atoms in this unit as Au-4) as demonstrated in Figure 1. Each Se atom makes a bond with 2-coordinated Au atoms in one side and with 4-coordinated Au atoms in the other side simultaneously. These Au-Se bonds build up rods of infinite length parallel to the b-direction. Each rod is connected by very weak AuAu and Se...Se interactions. The bond distances are 2.43 Å and 2.48 Å in linear and square-planar of Au-Se units, respectively. Furthermore, the Au-Au and Se-Se distances within a rod range from 3.49 Å to 3.71 Å and from 3.32 Å to 3.71 Å, respectively. The Au...Au and Se...Se contact distances between rods are of the same order as within the rods.

**Figure 1.** Projection of the structure of α -AuSe along the a-axis.**Figure 2.** Projection of the structure of β -AuSe along the a-axis.

Each Au is surrounded by six Se atoms, and vice versa, in the form of a distorted octahedron in β -AuSe. β -AuSe also contains two different Au atoms, which are bonded with two (*i.e.*, Au-2, Se-2) and four Se atoms (*i.e.*, Au-4, Se-4) to form linear and square-planar coordinations, respectively. Figure 2 clearly illustrate two different Au sites. The bond distances of Au-Se in linear and square-planar sites are 2.43 Å and 2.49 Å, respectively. The shortest Se...Se distance in this compound is 3.665 Å, which is still shorter than the van der Waals radii sum of Se (*i.e.*, 4.0 Å).

Results and Discussion

The results of EHTB band electronic structure calculations for α - and β -AuSe are presented in Figures 3 and 4, respectively, which plots the total density of states and the projected DOS for the 5d orbitals of Au. The dotted line in the figures refers to the Fermi energy. The band gaps of α - and β -AuSe are about 0.6 eV and 0.7 eV, respectively, which is in agreement with their semiconducting properties.

Figures 3(b), 3(c), and 3(d) represent the partial DOS for the 5d orbitals of Au-2, Au-4, and the 4s, 4p orbitals of Se in α -AuSe, respectively, as a function of energy. Also illustrated in Figures 4(b), 4(c), and 4(d) are the partial DOS calculated for the 5d orbitals of Au-2, Au-4, and 4s, 4p orbitals of Se in β -AuSe. The top portion of the occupied bands of both α - and β -AuSe is dominated by the Se orbital contribution, while the contribution of the 5d orbitals of Au occurs in the energy region well below the Fermi level. From the intensity and the area of the main peak around -15 eV in Figures 3(b), 3(c), 4(b), and 4(c), which represent the d-orbital contribution, it is noticed that the electron density contribution by the Au-2 d-orbitals is similar to that of the Au-4 d-orbitals. It is also shown by the Figures 3(b), 3(c), 4(b), and 4(c) that the electron density contribution from Au-2 and Au-4 d-orbitals in the region of the Fermi energy is nearly zero (only very weak Au-4 d-orbital contribution is seen in the energy region slightly above the Fermi level). Thus, the electron densities on the Au-4 and Au-2 atoms are similar.

As mentioned earlier, the d-electron count scheme in transition metal compounds is based on the fact that the frontier orbitals are made up of the metal d-orbitals. Thus Au³⁺ (*i.e.*, d⁸) and Au⁺ (*i.e.*, d¹⁰) are true only when the metal d-orbitals lie higher in energy than do the ligand p-orbitals. However,

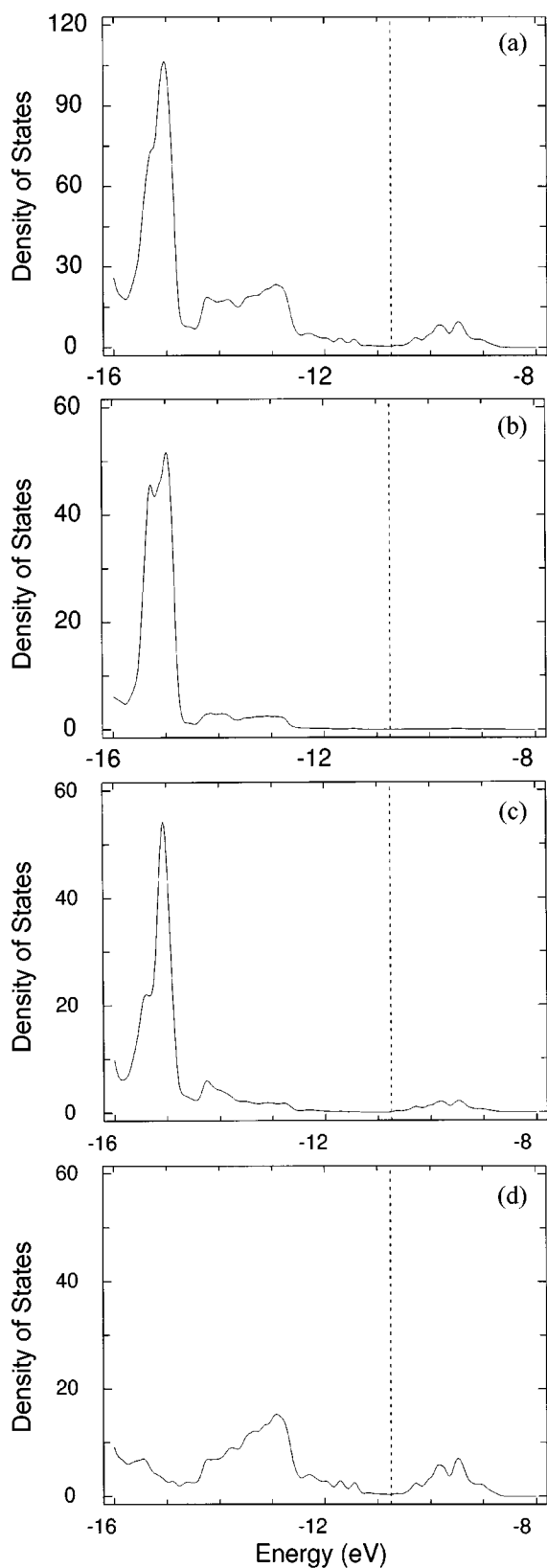


Figure 3. Total DOS (a) and projected DOS for the 5d orbitals of (b) Au-2, (c) Au-4, and (d) that of the 4s and 4p of Se in α -AuSe.

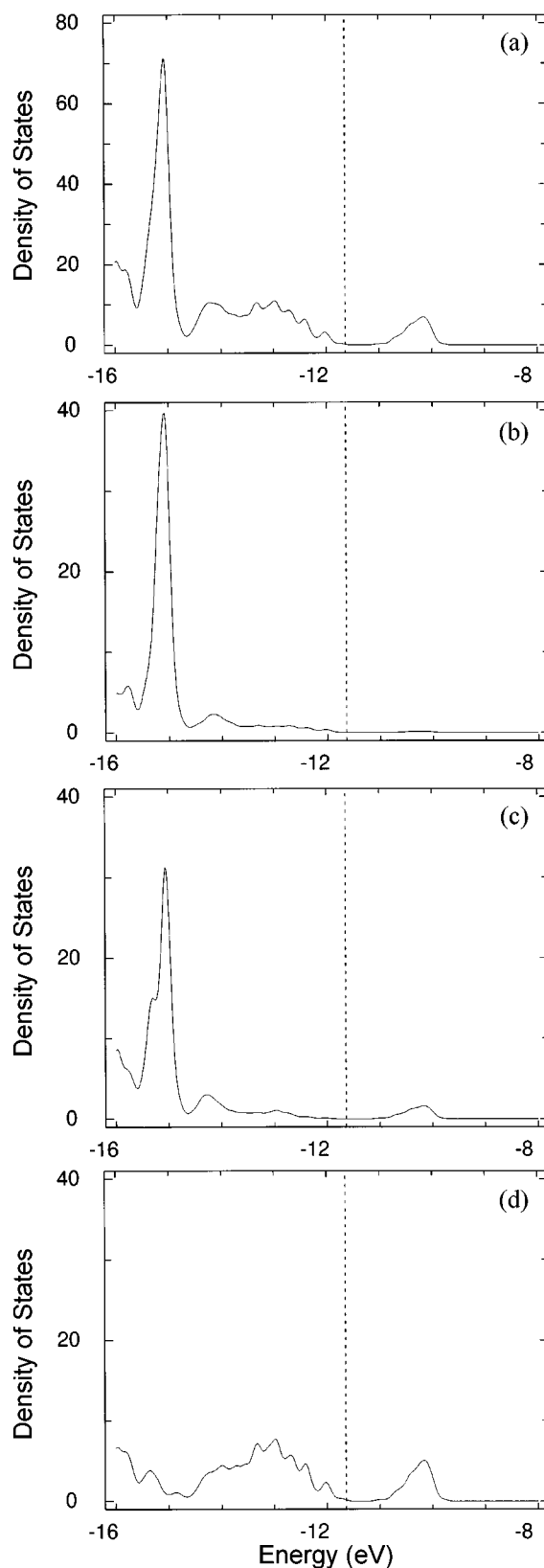


Figure 4. Total DOS (a) and projected DOS for the 5d orbitals of (b) Au-2, (c) Au-4, and (d) that of the 4s and 4p of Se in β -AuSe.

our EHTB calculations on total electron density show different results that d-orbital contributions lie well below the

Fermi level (see Figures 3 and 4). In addition, the Se orbital contribution is much stronger than the Au orbital contribu-

tion around the Fermi level, which represents the conduction band region (see Figures 3(d) and 4(d)). Since the energy levels of Au d-orbitals are lower than those of Se p-orbitals, the valence band (*i.e.*, HOMO) has stronger Au d-orbital character while the conduction band (*i.e.*, LUMO) has stronger Se p-orbital character. This is the reason why the frontier orbitals are majorly made up of Se p-orbitals in α - and β -AuSe. In this condition, electrons in higher energy (*i.e.*, Se p-orbitals) flow down to the orbitals in lower energy (*i.e.*, Au d-orbitals). Therefore, the oxidation states of two different Au become both close to Au⁺ (*i.e.*, d¹⁰) and Au environments in α - and β -AuSe should be described by [Au₂²⁺(Se)₂²⁻]. The shorter SeSe and AuAu distances in both α - and β -AuSe strongly support this description. Our result is in good agreement with the recent X-ray absorption spectroscopy study on AuSe that all Au in the compound show a monovalent state independent of their chemical environments.¹¹

Conclusions

Two gold chalcogenides, α - and β -AuSe, were known as mixed valence compounds having linear and square-planar units simultaneously. It is known that two different Au units show different Au environments: the oxidation states of Au in linear AuSe₂ and square-planar AuSe₄ units are +1 and +3, respectively. However, our EHTB calculations show that the oxidation states of Au in linear and square-planar units are both close to +1. This is because the frontier orbitals are largely made up of p-orbitals of chalcogen and halogen. Our results are consistent with the recent X-ray absorption spectroscopy study on AuSe in which all Au in

the compound show a monovalent state independent of their chemical environments.

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