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XPS and DFT studies of the electronic structures of AgAuS and Ag_3AuS_2

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ABSTRACT

X-ray photoelectron spectra of core levels and the valence bands were acquired, and the density-of-states (DOS) were calculated using periodic density functional theory (DFT) for synthetic ternary compounds AgAuS and Ag_3AuS_2, known as minerals petrovskaite uytenbogaardtite, respectively, for the first time. The chemical shift of the Au 4f binding energy as large as 0.65 eV relative to bulk elemental gold was found for Ag_3AuS_2, in contrast to only about 0.3 eV for AgAuS. The DFT analysis showed, in particular, that the S 3p states are largely pushed out from the Ag 4d and Au 5d bands affording two sub-bands in the valence region of both substances, but the overlapping of the S 3p and Au 5d states is larger for Ag_3AuS_2. It was demonstrated that the energy position of Au 4f levels is mainly influenced by Au–Ag interaction, and increasing the number of Ag atoms in the first coordination shell of S–Au–S units on going from AgAuS to Ag_3AuS_2 results in the positive shift of the Au 4f bands consistent with the experimental data.

1. Introduction

Gold and silver compounds with sulfur are of interest for many applications, such as mineralogy, geochemistry and mineral processing [1–15], materials science and nanotechnology, including solid electrolytes (see, for example [16–18] and references therein), resistive switches [19], metal sulfide nanoparticles and thiol-protected metal nanoparticles [20–24], sulfur layers and self-assembled thiol monolayers on metal surfaces [25–27]. There exist two ternary compounds close to Ag_3AuS_2 and AgAuS stoichiometry in the Au–Ag–S system at low temperatures, in addition to binary Ag_2S, Au_2S, AuS, Au_2S_3 substances and a range of the solid solutions [2–8]. The Ag–Au minerals uytenbogaardtite (Ag_3AuS_2) and petrovskaite (AgAuS) were found in many natural occurrences [1,9–13], and their characteristics are important for understanding the genesis of precious metals in the ore deposits and the behavior in the processes of their recovery.

Several crystalline structures of the ternary sulfides have been revealed [1–13,28,29]; in each of them Au atoms are coordinated by two S atoms at a distance of 2.33–2.36 Å with S–Au–S angle of 180°, whereas the crystallographic positions of Ag and S may vary. In the low-temperature AgAuS phase, the sublattice of sulfur atoms was found to have a strongly distorted body-centered cubic packing; three-quarters of silver atoms are surrounded by tetrahedrons of sulfur atoms, while the rest of silver may substitute the linearly coordinated Au atoms [28]. Cubic, tetragonal and trigonal crystalline modifications of natural and synthetic phases close to Ag_3AuS_2 composition, probably having similar chemical bonding, have been described in the literature. In particular, Seryotkin et al. [29] synthesized and studied single crystals of trigonal $Ag_{2.94}Au_{1.06}S_2$ phase and found that is constructed of the rigid linear S–Au–S groups, Ag atoms surrounded by four S atoms (of four different linear groups), and the S^{2-} anions having six bonds to Ag^+ and one bond to Au^+.

To the best of our knowledge, the electronic structures of the stable gold–silver sulfides have been not examined using quantum-chemical calculations and spectroscopic techniques, including X-ray photoelectron spectroscopy (XPS), until now. Photoelectron spectra have been measured, and the band structure and density-of-states (DOS) of binary silver chalcogenides have been calculated in many investigations [16–19], but there are only a few studies on Au_2S. Ishikawa et al. [30] have reported that the cuprite-type Au_2S is a p-type semiconductor with the activation energy of 0.37 eV, although the conductivity can be described by a random hopping model. The gap width values (direct or indirect) reported for Au_2S are controversial, varying in the range 2.6–0.5 eV [23–25,31–33]. Recently Pryadchenko et al. [34] have measured X-ray emission Au $L\beta_5$ and Au L_3-edge absorption spectra and used DFT

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to calculate DOS of the valence band and the conduction band of Au_2S. The state of Au and S atoms in the gold sulfides and surface layers of sulfur on gold derived from the photoelectron spectra is debatable. The low chemical shifts of both Au and S core level spectra relative to the elements have been observed and ascribed to a small electron density transfer from Au to S atoms [23,25]. Alternatively, this was interpreted in terms of decomposition of the surface layer of the metastable sulfide phase yielding Au nanoparticles with polysulfide-type adlayer [35].

Here, we report for the first time the results of X-ray photoelectron spectroscopy and DFT calculations for AgAuS and Ag_3AuS_2 compounds. The surface layers of the sulfidic materials exposed to air and X-ray irradiation were proved to be quite stable, and the spectra reflected differences in electronic structures of these phases, which were explained employing DFT simulations.

2. Materials and methods

Silver–gold sulfides AgAuS and Ag_3AuS_2 were prepared by fusing the elements in stoichiometric amounts via procedures reported in detail elsewhere [6,28,29]. In brief, the synthesis was conducted in evacuated quartz ampoules heated for 3 days at a rate of 0.2–0.5 °C/min to 1050 °C and kept for 12 h, and then cooled to 150 °C and annealed for 30 days. After the annealing, the ampoules were cooled to room temperature for about 7 h. The petrovskaite samples have the composition of $Ag_{0.94}Au_{0.85}S$ and rare 2–5 μm inclusions close to $Ag_{2.6}Au_{0.9}S_2$, according to the microprobe analysis [28]. The composition of uytenbogaardtite samples can be represented as $Ag_{3.1}Au_{0.9}S_2$ [29]. Below, the substances are denoted as AgAuS and Ag_3AuS_2 for simplicity. The XRD studies showed that the synthetic AgAuS and Ag_3AuS_2 are identical to low-temperature petrovskaite and uytenbogaardtite phases ([36], cards 19–1146 and 20–461, respectively). The petrovskaite had a crystalline lattice with the space group $R\bar{3}m$ and the parameters $a = 13.4235$ Å, $c = 9.0873$ Å, $V = 1418.07$ Å^3, $Z = 24$ [28]. The uytenbogaardtite Ag_3AuS_2 was determined to occur as a trigonal phase, space group $R\bar{3}c$, with the unit cell parameters $a = 13.7104$ Å, $c = 17.1170$ Å, $V = 2786.50$ Å^3, $Z = 24$ [29].

XPS experiments were carried out with a SPECS instrument equipped with a hemispherical analyzer PHOIBOS 150 MCD 9 at electron take-off angle 90°. Pass energies were 8 eV for high resolution spectra of all major lines excited using a monochromatic Al Kα source (1486.7 eV) and 20 eV for survey spectra excited also, for higher sensitivity, with unmonochromatized Mg Kα line (1253.6 eV) of the X-ray tubes. The analytical chamber vacuum was $1 \cdot 10^{-9}$ mBar or better. A scanning ion source PU-IQE 12/38 operating at the accelerating voltage 2.5 kV and ion current 15 μA was used for Ar^+ sputtering of the sample surfaces. The binding energy scale was referenced to the C 1s line of adventitious aliphatic carbon (285.0 eV); the low energy electron flood gun was applied to eliminate inhomogeneous electrostatic charging when it was necessary. The shift caused by the charging could be as big as about 2 eV for AgAuS, while the charging of Ag_3AuS_2 specimens was negligible. The spectra were recorded several times from different specimens; the uncertainty in BEs was within ±0.1 eV, depending on a specific line, sample nature and handling. The experiments were performed on compact specimens as received in the synthesis and stored in atmosphere, their fracture surfaces prepared in air (unfortunately, we had no facilities for this in the spectrometer), and specimens ground to 100–200 μm particles in a jasper mortar, attached to a conductive carbon sticky tape and immediately transferred to the vacuum chamber. The finely ground samples were found to be the least oxidized, probably, because fracture of polycrystalline lumps exposed grain boundaries oxidized during synthesis or storing, so the spectra presented in this paper were acquired from the freshly ground materials. The lines were fitted with Gaussian–Lorentzian peak profiles after Shirley background subtraction using CasaXPS software. The spin–orbit splitting energies for S $2p_{3/2,1/2}$ and Au $4f_{7/2,5/2}$ doublets were taken to be 1.19 eV and 3.67 eV, the components had intensity ratios 2:1 and 4:3, respectively, and equal linewidths.

DFT calculations were carried out using the plane wave pseudopotential method as implemented in the Quantum Espresso code [37]. The generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [38] was used to calculate exchange–correlation energy. The core–valence interaction was taken into account through ultrasoft pseudopotentials [39] (for Ag, Au and S atoms we used Ag.pbe-dn-rrkjus_psl.0.1.UPF, Au.pbe-dn-rrkjus_psl.0.1.UPF and S.pbe-n-rrkjus_psl.0.1.UPF pseudopotentials, correspondingly, from the Quantum Espresso library, see www.quantum-espresso.org/pseudopotentials) that include scalar-relativistic effect for all atoms. A 30 Ry wave function cutoff and 240 Ry charge density cutoff were considered, while the Brillouin zone was sampled using a 2 × 2 × 2 Monkhorst Pack grid for optimization of structural lattice parameters. An extended 4 × 4 × 4 Monkhorst Pack grid was utilized in calculating the forbidden band gaps. A primitive lattice unit cell containing eight formula units was used for geometry optimization of AuAgS structure. The optimization resulted in slightly overestimated cell parameters with $a = b = 8.43$ Å, $c = 8.41$ Å and $\alpha = \beta = \gamma = 107.6°$ as compared with the experimental cell parameters of $a = b = c = 8.32$ Å and $\alpha = \beta = \gamma = 107.5°$ in Ref. [28]. For optimization of Ag_3AuS_2, a primitive lattice unit cell with 9 gold, 23 silver and 16 sulfur atoms was taken. These calculations also resulted in slightly overestimated cell parameters ($a = 9.83$ Å, $b = 9.80$ Å, $c = 9.84$ Å, $\alpha = 88.9°$, $\beta = 88.8°$, $\gamma = 88.7°$), which have to be compared to parameters of the experimental structure [29] with $a = b = c = 9.76$ Å and $\alpha = \beta = \gamma = 89.3°$.

To elucidate factors affecting energy positions of core Au 4f levels, cluster calculations have been carried out in scalar relativistic Douglas–Kroll–Hess approach [40] using the linear combination of Gaussian-type orbitals fitting-function density functional (LCGTO-FF-DF) method [41] as implemented in the parallel program ParaGauss [42]. Contracted in generalized fashion all-electron Gaussian-type basis sets as in previous cluster scalar relativistic calculations of silver and gold species [43,44] have been utilized: (21s,17p,11d,7f) → [11s,10p,7d,3f] for Au; (18s13p9d) → [7s6p4d] for Ag, (12s9p2d) → [6s4p2d] for S atoms.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

The survey spectra (Fig. 1) show that the sample surfaces contained no impurity elements except for carbon and oxygen, with the high-resolution C 1s and O 1s lines (see Electronic Supplementary Information, ESI) being characteristic of hydrocarbons and oxygen-bearing carbon compounds (mainly COH groups), adsorbed water and hydroxyl groups inevitable for materials exposed to atmosphere. No oxygen and carbon components attributable to metal oxides and carbonates were found in the spectra from freshly crushed Ag–Au sulfides. The atomic ratios of silver, gold and sulfur (Table 1) are in reasonable agreement with the bulk composition of AgAuS and Ag_3AuS_2 substances.

The Ag $3d_{5/2,3/2}$ doublet bands from the substances are rather symmetric and narrow, with the Ag $3d_{5/2}$ peaks being centered at a binding energy (BE) of 368.0 ± 0.05 eV for AgAuS and at 368.15 eV for Ag_3AuS_2. It is known that the higher negative chemical shift in BE of Ag 3d lines usually corresponds, in opposite to a majority of elements, to the larger positive charge localized at Ag atoms [45]. This signifies therefore that Ag(I) entities have more positive charge in AgAuS than in Ag_3AuS_2. Interestingly, the position of Ag $3d_{5/2}$ at 368.0 eV for Ag_2S (ESI, see also [15,17,45]) is closer to the value for AgAuS. The Auger Ag $M_4N_{45}N_{45}$ maxima were found to have the kinetic energies of 356.7 ± 0.15 eV for both Ag_3AuS_2 and AgAuS, whereas those are situated at 357.6 eV for Ag

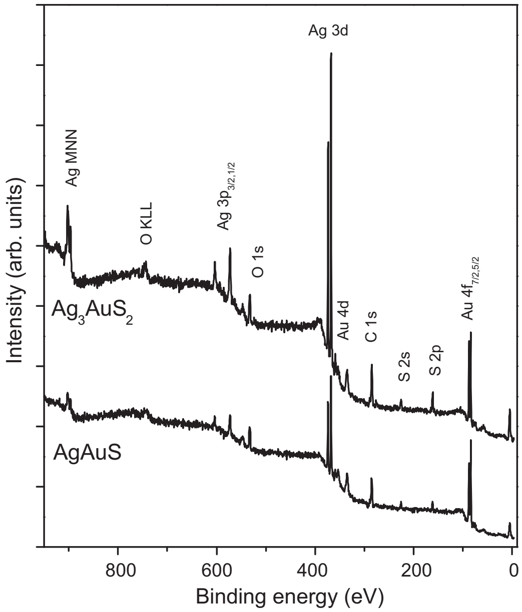

Fig. 1. X-ray photoelectron survey spectra acquired using Mg Kα line excitation from freshly ground AgAuS and Ag_3AuS_2 specimens.