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Anomalous Chemical Shifts in X-ray Photoelectron Spectra of Sulfur-Containing Compounds of Silver (I) and (II)†

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Anomalous chemical shifts, *i.e.* cases when binding energy decreases with the increase f the oxidation state, have been well-documented for selected compounds of silver, and well understood based on analysis of initial- and final-state effects in the XPS spectra. Here we report two examples of even more exotic behaviour of chemical shifts for two silver compounds. The first one is $Ag_2S_2O_7$ which exhibits both positive and negative substantial shifts with respect to metallic Ag for two distinct Ag(I) sites in its crystal structure, which differ by as much as 3.4 eV. Another is $AgSO_4$, a rare example of oxo silver (II) salt, which exhibits "normal" chemical shift but the Ag $3d_{5/2}$ binding energy takes the largest value measured for a silver(II) compound (370.1 eV). This property is connected predominantly with the extremely strongly oxidizing nature of Ag(II) species.

Introduction

Since silver is a key catalyst in several industrial oxidation processes, oxygen states on silver surfaces[1,2,3] and silver oxides[2,3,4,5,6,7,8,9,10,11,12] have been extensively characterised by means of X-ray photoelectron spectroscopy (XPS). This surface-sensitive method was also applied for monitoring of thermal decomposition of silver oxides[2,6,7] and silver (I) carbonate[13]. One interesting feature of XPS spectra of Ag-O systems is that binding energy (BE) of silver 3d electrons decreases in the sequence Ag(0) > $Ag(I)_2O$ > Ag(III) site in AgO (*i.e.* $Ag(I)Ag(III)O_2$)[14] – contrary to what should be expected from simple electrostatic considerations. The difference of binding energies ($Ag3d_{5/2}$) between Ag and Ag(III) site in AgO reaches as much as 1.40 eV. A similar albeit less pronounced effect has been observed for silver fluorides where the chemical shift ($Ag3d_{5/2}$) measured for Ag(I)F is more positive (by 0.35 eV) than that of a freshly prepared $Ag(II)F_2$[15,16]. Analogous tendency has been noticed for selected compounds of Cd, Co, Cu, Ba etc.[17] Understanding of this phenomenon is important, since negative shifts often overlap with "normal" systematic chemical shifts for multicomponent samples or those which decompose easily in the UHV conditions of XPS experiment, thus rendering analysis of the spectra very difficult. In principle, there are many possible mechanisms which can lead to atypical behaviour, as outlined in an excellent overview of diverse initial- and final-state phenomena in the XPS spectroscopy.[17] One major factor responsible for negative chemical shifts is the Madelung potential, which is always negative at a cation site (due to surrounding anions)[18]. It appears to be the dominant factor in the case of Ag oxides, where positive shift due to electron loss is small (due to the 5s orbital being large and diffuse[11]) and overcome by the significant negative shift due to the Madelung potential.

In this work we show that even more complex manifestations of both effects are possible as exemplified by $Ag_2S_2O_7$, a Ag(I) compound with two distinct Ag(I) sites in its crystal structure. Both sites exhibit very different Ag $3d_{5/2}$ BEs thus pointing out to different Madelung energies for both crystal sites, which is in agreement with the diverse ligand environments of both Ag(I) cations as seen from crystallographic data, and with the results of the dft calculations. We also report for the first time the XPS spectrum of silver (II) sulfate ($AgSO_4$) – an unusual magnetic semiconductor containing Ag(II) cations[19]. We show that the Ag $3d_{5/2}$ BE in this compound reaches the value of 370.1 eV which is the largest ever measured for a compound of Ag(II). We link this property to super-strongly oxidizing nature of Ag(II) species in sulfate environment. Importantly, the Bes for Ag(II) in oxo-ligand environment have not been reported so far in the literature since Ag(II) disproportionates to Ag(I) and Ag(III) in simple oxides (*e.g.* $AgO = Ag(I)Ag(III)O_2$). Our own interest in higher oxidation states of silver is motivated by the fact that compounds of Ag(II) and Ag(III) share many similarities with oxocuprates and could perhaps constitute a novel family of superconductors[20].

Experimental

Synthetic procedures, description of the XPS system, sample preparation, spectra referencing procedure, quantitative analysis of the elemental contents, the as-measured XPS spectra for all

systems studied, analysis of the spectra for three important reference systems (Ag, Ag_2O, AgO), as well as BEs for S and O, are presented in the ESI. The quantum mechanical calculations were performed with CASTEP[21] to estimate Madelung effects at silver sites. We have applied density functional theory (DFT) and the generalized gradient approximation (GGA) with the PBEsol exchange-correlation functional (adapted for solids), the energy cutoff of 600 eV, and k-point grid of 0.07 $Å^{-1}$ (*cf.* ESI). Primitive cells of $Ag_2S_2O_7$ (Z=2),[22] $AgSO_4$ (Z=8)[23] and Ag_2SO_4 (Z=4)[24] were computed.

Results and discussion

XPS spectra of $Ag_xS_yO_z$ compounds. Of $Ag_xS_yO_z$ compounds, only Ag_2SO_4 has been previously studied by XPS[25,26] and some of the compounds described in this work were, to our knowledge, analysed by XPS for the first time (see Table 1 for the full list of BEs of all compounds studied here).

Silver (I) sulfate (ESI 6.4). Elemental composition of the surface of Ag_2SO_4 in ultra-high vacuum conditions exhibits significant oxygen deficiency – its stoichiometry is closer to Ag_2SO_3. The BEs are equal to 374.0 eV (Ag $3d_{3/2}$) and 368.0 eV (Ag $3d_{5/2}$), which is identical to the values reported by Kaushik[25]. As we will see, Ag_2SO_4 will serve as a valuable internal standard for the less stable phases.

Silver (I) hydrogen sulfate (ESI 6.5). The XPS spectrum of $AgHSO_4$ is very similar to that of Ag_2SO_4. Quantitative analysis shows excessive amount of sulfur, which can be attributed to traces of non-volatile H_2SO_4 remaining after the synthesis. Ag 3d bands are located at 374.1 eV (Ag $3d_{3/2}$) and 368.1 eV (Ag $3d_{5/2}$) – almost identical to those of Ag_2SO_4. However, this similarity is coincidental since the S 2p and O 1s bands appear at higher BEs than in the sulphate (*cf.* ESI).

Spectral analysis of fluorine-containing silver sulfates

Silver (I) triflate (trifluoromethanesulfonate) (ESI 6.7). Quantitative analysis of the $AgSO_3CF_3$ surface shows that it is deficient in elements forming the anion. This suggests a photoinduced decomposition involving *e.g.* release of triflate radical, $^{\bullet}SO_3CF_3$. Indeed, $AgSO_3CF_3$ is thermally unstable at T > 400 ^{o}C[27] and the decomposition of its surface is certainly accelerated in UHV conditions. The Ag 3d peaks appear at 374.5 eV (Ag $3d_{3/2}$) and 368.5 eV (Ag $3d_{5/2}$). These are somewhat higher than the corresponding values for the sulfate and hydrogen sulfate, and also higher than that for metallic silver, which can be traced back to the weakly-coordinating character of the triflate anion. Thus, positive shift of the BE due to electron loss is not fully compensated by the reverse effect from a stronger coordination by negatively charged anions.

Silver (I) fluorosulfate (ESI 6.6). Spectra of $AgSO_3F$ exhibit a characteristic evolution depending on the time the sample has been irradiated with X-rays (**Figure 1**).

$AgSO_3F$ is known to decompose at temperatures above 270°C according to the following reaction equation[27]:

$$2AgSO_3F \rightarrow Ag_2SO_4 + SO_2F_2 \uparrow \quad \text{(Eq.1)}$$

Since a gaseous product (sulfuryl fluoride) is formed during decomposition, this process is more favoured in ultra-high vacuum conditions of the XPS system and proceeds even at ambient temperature.

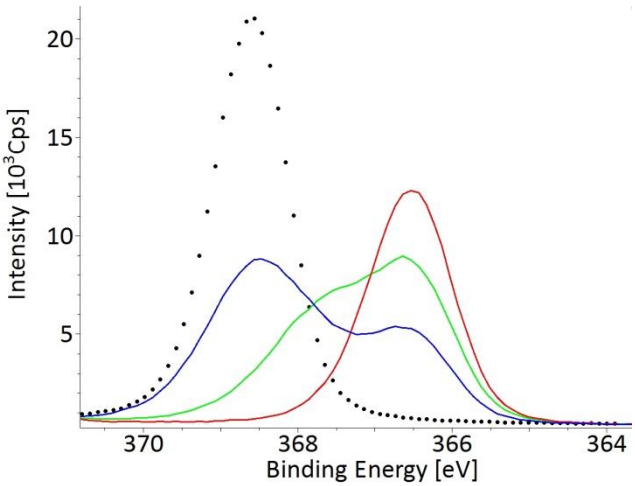

Figure 1. Evolution of Ag $3d_{5/2}$ band of $AgSO_3F$ in time: a) as-obtained (red line); b) after 1 hour of irradiation (green); after 4 hours of irradiation (blue); dotted black line - the XPS spectrum of Ag_2SO_4 for comparison. BE as measured.

	Ag $3d_{5/2}$	Ag $3d_{3/2}$
Ag_2SO_4	368.0[#]	374.0
$AgHSO_4$	368.1	374.1
$AgSO_3F$*	366.2	372.2
$AgSO_3CF_3$†	368.5	374.5
$AgSO_4$*	370.1	376.1
$Ag_2S_2O_7$*	369.3 365.9	375.3 371.9

Table 1. Comparison of XPS binding energies of silver compounds studied in this work. All values given in eV and referenced to C 1s line of inadvertent carbon contamination (284.6 eV), except: †F 1s line of $NaSO_3CF_3$ (688.2 eV)[24], *Ag $3d_{5/2}$ line of Ag_2SO_4 internal standard (368.0 eV). #The literature value 368.0 eV.[25]

Ag_2SO_4 as an internal standard for unstable $AgSO_3F$

Analysis of the spectra shown in Fig. 1 indicates that the decomposition process of $AgSO_3F$ triggered by X-rays and UHV conditions leads to the formation of surface Ag_2SO_4 species. This is further supported by quantitative analysis of the initial spectrum and the spectrum obtained after several hours of irradiation (ESI 6.6.1 and 6.6.4). The irradiated sample is richer in Ag but it has lower content of S and O – in agreement with the reaction equation (Eq.1). Having identified the higher-BE component in the Ag 3d spectrum of the irradiated sample as Ag_2SO_4, we may use it as an internal standard to determine the BEs of various spectral features of $AgSO_3F$. The calibrated Ag 3d BEs of the fluorosulfate are 372.2 eV (Ag $3d_{3/2}$) and

366.2 eV (Ag $3d_{5/2}$), *i.e.* almost 2 eV smaller than those for Ag_2SO_4 (Table 1). Such an appreciable negative shift of the BEs can possibly be explained by the fact that the Ag(I) cation is surrounded by as many as 6 ligands at short separation (5 O atoms at 2.42-2.55 Å and 1 F atom at 2.61 Å) for $AgSO_3F$[27] but by only 4 O ligands (at 2.4–2.44 Å) for Ag_2SO_4,[24,28] (**Figure 2**) hence the Madelung energy at cationic site is much larger for the former compound.

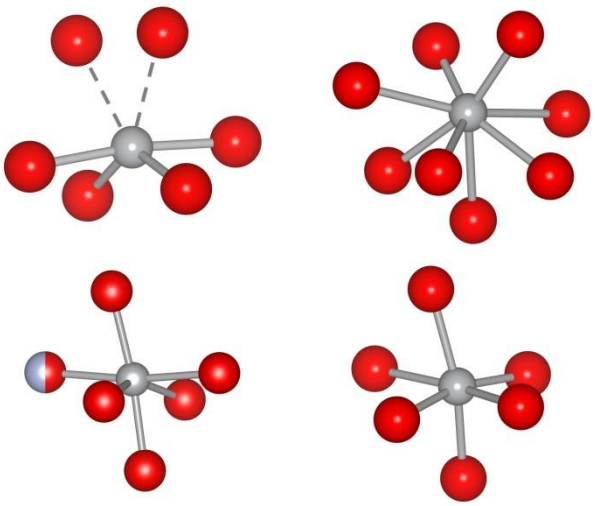

Figure 2. The first coordination sphere of Ag(I) in: Ag_2SO_4 (top left), $AgSO_3F$ (bottom left), and for two distinct crystallographic sites of $Ag_2S_2O_7$ (right, top and bottom).

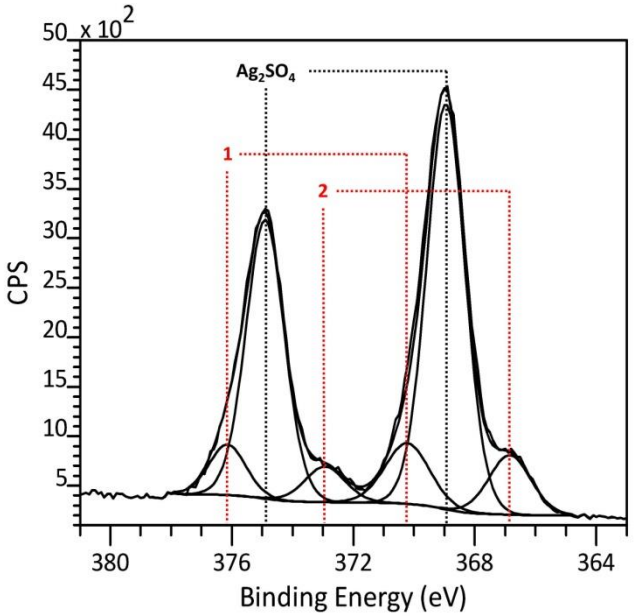

Figure 3. The Ag 3d bands measured for $Ag_2S_2O_7$ and showing three components each. The middle component originates from Ag_2SO_4, while the two smaller components (1&2) are assigned to Ag(I) of $Ag_2S_2O_7$ in two non-equivalent crystallographic sites. BE as measured.

Decomposition of silver (I) disulfate and silver (II) sulfate as monitored by XPS

Silver (I) disulfate (ESI 6.9). The crystal structure of silver(I) disulfate has been determined only recently.[22] This compound decomposes thermally at temperatures above 230°C[19]:

$$Ag_2S_2O_7 \rightarrow Ag_2SO_4 + SO_3 \uparrow \quad \text{(Eq.2)}$$

Similarly to $AgSO_3F$, a gaseous product is formed in this reaction, which is even more favourable under UHV conditions. The Ag 3d bands in the XPS spectrum measured for the as-obtained $Ag_2S_2O_7$ (**Figure 3**) indicate that decomposition has already occurred to large extent at the surface, which resulted in the bands being broad and asymmetric. The survey spectrum of the as-obtained disulfate sample shows that its composition resembles more that of Ag_2SO_4, again suggesting that the majority of the disulfate has decomposed at the surface. A closer look at the Ag 3d bands of the sample reveals a complex system of three components (Figure 3).

The predominating component is assigned to Ag_2SO_4 – the final product of decomposition. The two remaining smaller features (labelled **1** and **2** in the Figure 3) have nearly identical integrated intensities and we assign them to two non-equivalent silver (I) cations in the crystal structure of $Ag_2S_2O_7$[22]. In the first of these sites, silver is coordinated by six O atoms in a form of a slightly deformed octahedron (at 2.31–2.50 Å, Figure 2), similar to that found for $AgSO_3F$. Such a symmetrical strong binding to 6 O atoms results in a low Ag 3d binding energy due to Coulombic effects especially that the average distance from Ag to 6 ligands is much shorter for $Ag_2S_2O_7$ (2.42 Å) than for $AgSO_3F$ (2.51 Å). Indeed, the BE (Ag $3d_{5/2}$) for this Ag(I) site in $Ag_2S_2O_7$ (365.9 eV) is even slightly smaller (by 0.3 eV) than that measured for $AgSO_3F$ (366.2 eV). Simultaneously, the other independent Ag(I) cation in $Ag_2S_2O_7$ is coordinated by eight O atoms (Figure 2) at the average Ag-O distance of 2.69 Å, *i.e.* much larger than for the octahedral site (2.42 Å). This must lead to small Coulombic effects and therefore the BE for this site should be shifted to positive energies. Indeed, the BE for this site equals 369.3 eV, hence it is upshifted by 1.3 eV with respect to Ag_2SO_4. According to our best knowledge, such a large split of the core-state BEs (3.4 eV) for a given cation with two different coordination numbers (here, CN=6: more covalent bonding, CN=8: more ionic bonding to ligands) found in the same chemical compound, has never been reported before. We will return to this feature in the last section.

Silver (II) sulfate (ESI 6.8). The survey scan of as-obtained $AgSO_4$ reveals that the surface is deficient in oxygen (ESI). Indeed, $AgSO_4$ decomposes at ambient pressure conditions at temperature as low as 110°C, releasing oxygen and yielding $Ag_2S_2O_7$[19,22]:

$$2AgSO_4 \rightarrow Ag_2S_2O_7 + \frac{1}{2}O_2 \uparrow \quad \text{(Eq.3)}$$

The decomposition can be substantially accelerated by *in situ* heating of the sample up to 50 °C.

In order to assign the Ag 3d BEs of $AgSO_4$, its thermal decomposition was monitored by registering XPS spectra on progressive heating of the sample (**Figure 4**). The high-BE

component decreases in time, while the lower-BE component becomes more prominent. At the same time, the entire spectrum

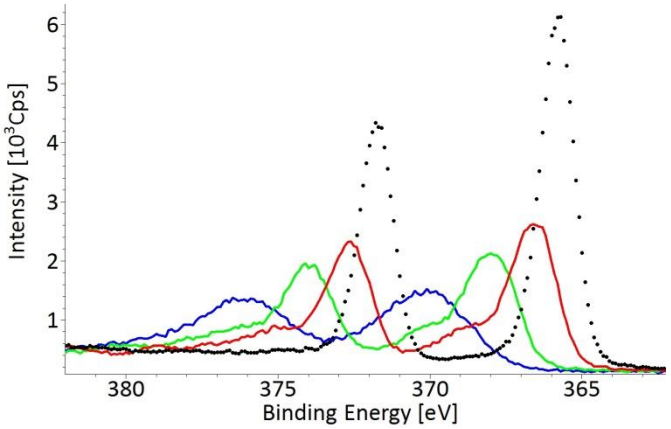

Figure 4. Evolution of Ag 3d bands of $AgSO_4$ in time: as-obtained (25 °C, blu line), after heating to 35°C (green), after heating to 45°C (red), after heating to 50°C (dotted black line). BE as measured.

shifts towards lower binding energies. This can be explained by negative charging caused by electron flood gun since the possible decomposition products ($Ag_2S_2O_7$ and Ag_2SO_4) are broad band gap (colourless) insulators. After reaching 50°C, both the elemental composition and the relative positions of Ag 3d, S 2p and O 1s bands indicate that the final reaction product is Ag_2SO_4. The sample was further heated up to 120°C, but no other changes to the spectra (except for continuing negative BE shift) were observed. Thus, the decomposition reaction of $Ag(II)SO_4$ in UHV seems to lead directly to $Ag(I)_2SO_4$ and omitting the disulfate intermediate. This can be understood assuming that the *in situ* formed thin layer of disulfate is very reactive and its subsequent decomposition according to reaction equation (Eq.2) is facile at the conditions of experiment.[29]

Like previously for $Ag_2S_2O_7$, we have used Ag_2SO_4 as an internal reference and determined the Ag 3d BE values. $AgSO_4$ is characterised by very high BEs: 376.1 eV (Ag $3d_{3/2}$) and 370.1 eV (Ag $3d_{5/2}$). These are the largest BE values of all the $Ag_xS_yO_z$ compounds that we have studied in this work (**Figure 5**). Moreover, the BE of 370.1 eV is the largest (Ag $3d_{5/2}$) chemical shift for a Ag(II) species ever reported. For example, the corresponding values for the Ag(II) tetraphenylporphyrin and Ag(II) octaethylporhyrin are 367.6 eV and 368.3 eV,[30] thus by more than 1 eV smaller than that for $Ag(II)SO_4$. The (Ag $3d_{5/2}$) chemical shift for $AgSO_4$ is larger even that those for selected compounds of Ag(III), such as $KAgF_4$ (368.35 eV)[16], and it is surpassed only by the corresponding value for Ag(III) octaethylporphiryne perchlorate (371.0 eV)[30] and for the record-holding ethylenebis(biguanide)silver(III) persulfate (371.4 eV).[31]

Such a large value of BE (Ag $3d_{5/2}$) for $Ag(II)SO_4$ can certainly be traced back to the very large positive BE shift as the oxidation state of silver increases from (I) to (II) (*cf.* ESI, and the next section); apparently, this contribution is not compensated by the Coulombic effect from ligands, despite the fact that the four Ag-O distances of the $[AgO_4]$ plaquettes are quite short in this compound (2.05–2.20 Å).[23] The valence states of silver must also experience large "positive shifts" of BEs; indeed, $AgSO_4$ – just like all Ag(II) compounds[20] – is an extremely powerful oxidizer. Notably, Ag(II) ions solvated in anhydrous sulphuric acid exhibit formal redox potential of +2.9V *vs.* NHE, which renders them the strongest fluorine-free oxidizer known to day.[32] This feature originates from the huge second ionization potential of Ag, which exceeds even those of many non-metals,[20] and leads to unusual redox chemistry of Ag(II) salts with oxo ligands.[19,22,33]

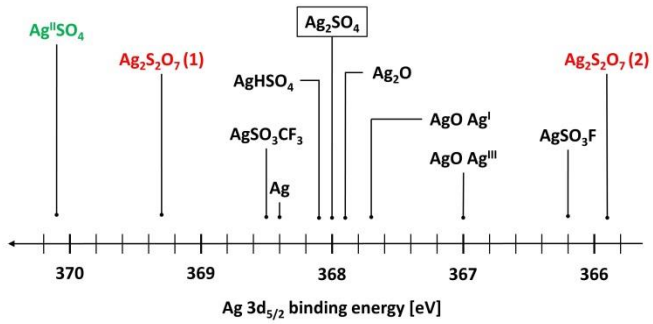

Figure 5. Graphic representation of Ag $3d_{5/2}$ BEs of AgO_x, $Ag_xS_yO_z$ and $Ag_xS_yO_zF_n$ compounds investigated in this work.

Coulombic effects on Ag $3d_{5/2}$ BEs for silver (I) disulfate and silver (I) and (II) sulphates: DFT calculations

In an attempt to explain the two intriguing features of the XPS spectra of $Ag_2S_2O_7$ (*i.e.* Ag $3d_{5/2}$ BEs differing by 3.4 eV for two different Ag(I) sites) and $AgSO_4$ (*i.e.* the largest measured Ag(II) $3d_{5/2}$ BE of 370.1 eV) we have presented a number of qualitative arguments linked to crystal structures of compounds studied as well as impact of progressive ionization on the oxidizing properties of silver species. A fully quantitative analysis of BEs must take into account both the initial- and the final-state effects;[8] however, it has been argued that the initial state effects usually have the largest impact on the BE values.[34,35,36,37] One extremely useful method of analysing the BE values relies on Wagner's method of Auger parameter analysis.[38] Regretfully, due to inherent instability of the surface of the compounds studied here under UHV conditions we could not achieve satisfactory compromise between quality of the spectra and time needed for measuring both the core spectra in the Ag 3d region and the Auger region. Thus, we could not employ Wagner's method of Auger parameter analysis, which has proven useful in other works for more stable Ag compounds.[25] However, a careful study of samples' gradual decomposition combined with insights from previous studies of thermal decomposition of those Ag compounds gave us sufficient grounds to draw conclusions from the core level spectra alone.

A rigorous quantitative procedure exists of deriving the core level BE values based on calculations using a cluster model.[35] Here, we have attempted a much simpler semi-quantitative

estimation of coulombic effects while taking into account only the Mulliken charges on atoms (*i.e.* silver and its first oxo-coordination sphere) as computed using DFT (ESI).[39] By necessity, this approach cannot be extremely accurate but it can still give us insights into the anomalous effects observed for $Ag_2S_2O_7$ and $AgSO_4$.

Our DFT calculations show that the charge of approximately +0.55e resides on Ag(I) site in Ag_2SO_4, and a slightly larger charges of +0.64 to +0.66e are computed for Ag(I) sites in $Ag_2S_2O_7$ (ESI). These values should be compared with the one of +0.48e derived previously from XPS measurements for Ag_2O.[40] Indeed, Ag_2O is the most basic Ag(I) species in this series (and with the least ionic Ag–O bonding), $Ag_2S_2O_7$ is the most acidic one, while Ag_2SO_4 has intermediate character between the two. Thus, as the weakly-coordinating character of anion modestly increases in the series: $O^{2-} < SO_4^{2-} < S_2O_7^{2-}$, the iconicity of the Ag–O bonding also slightly increases in the same direction. On the other hand, the Mulliken charges on Ag(II) centers are close to +1e (ESI) and they compare well with that of +1.05e determined from XPS spectra for CdO.[40] Moreover, the charge on Ag(II) center is not far from the average of charges on Ag(I) and Ag(III) sites (+1.2e) as determined for $Ag(I)Ag(III)O_2$.[40] Thus, the Mulliken charge on silver center clearly increases by nearly 0.5e as the oxidation state increases. This direct coulombic effect which obviously links to the oxidizing properties dramatically increasing in the Ag(I) << Ag(II) series, seems to play a dominant role for the substantial increase of Ag $3d_{5/2}$ BE as one compares $Ag(II)SO_4$ *vs.* $Ag(I)_2SO_4$. This "normal" trend is similar, for example, to what has been observed for diverse vanadium oxides, where BEs have systematically increased for oxidation states of V increasing from +2 to +5.[41]

The Mulliken charges on O atoms are computed to fall in range between –0.78e and –0.88e for $Ag_2S_2O_7$, and they also take very similar values for $AgSO_4$ (from –0.81e to –0.84e) and Ag_2SO_4 (–0.84e). Thus, it is not the charge on oxide anions but rather their number as well as the Ag–O distances in the first coordination sphere of silver cations, which seem to have major impact on the coulombic effects at Ag sites. It turns out that these effects on BE are rather similar (ranging from –29.3 eV to –30.4 eV) for all silver cations adopting the quasi-octahedral environment (*cf.* ESI), be it only slightly distorted (as for 6-coordinated Ag(I) site in $Ag_2S_2O_7$), or more distorted (as for buttefly Ag(I) site in Ag_2SO_4), or even severely elongated (as a quasi-square planar Ag(II) site in $AgSO_4$). However, a very large difference of BEs (6.6 eV) originating from the first coordination sphere has been estimated for two distinct crystallographic sites of $Ag_2S_2O_7$ (ESI). Although the magnitude of this effect will be partly diminished by the impact of the second (positively charged) coordination sphere to the Madelung effects, yet this calculated difference seems to be large enough to constitute a major factor behind the large experimentally observed BE split (3.4 eV) for the less ionic quasi-octahedral and more ionic quasi-cubic Ag(I) sites.

Conclusions

We have determined for the first time the binding energies for Ag 3d (for S 2s, S 2p and O 1s see ESI) for several compounds of silver which had not been previously studied by XPS. For these which exhibit facile decomposition which results in $Ag(I)_2SO_4$, the BE (Ag $3d_{5/2}$) of the *in situ* formed Ag_2SO_4 has been used as a reference.

We were able to show that Ag 3d binding energies do not always follow the anomalous but simple pattern, noticed previously for various oxides and fluorides of silver, of the decreasing BE with the increasing oxidation state. The example of $Ag_2S_2O_7$ clearly shows that crystallographic environment can greatly influence the binding energies of Ag(I) cations, resulting in significant differences of BE even within the same compound; the difference of the core-state BEs is extremely large for two distinct cationic sites in the crystal structure of this compound (3.4 eV).

Finally, powerful $Ag(II)SO_4$ oxidizer[32] exhibits the largest measured BE value among all Ag(II) compounds studied so far (370.1 eV). This feature, which may be explained by the qualitatively "normal" effect of the increasing charge at the metal center as the oxidation state increases – yet the one with huge amplitude – adds to a long list of peculiar physicochemical properties exhibited by this unusual black narrow-band gap antiferromagnet.[19,22,23]

The results presented in this work also suggest that a more systematic analysis is worthwhile of the chemical shifts of silver for an even larger spectrum of its compounds.

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Notes and references

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† This work is dedicated to Prof. Jack Lord Lewis of Newnham at his 75th birthday.

‡ Electronic Supplementary Information (ESI) available: synthetic procedure, description of the XPS system, the unreferenced XPS spectra

for all systems studied, analysis of 3 reference spectra, and S 2s, S 2p and O 1s Bes, results of the DFT calculations. See DOI: 10.1039/b000000x/

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