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High-energy photoemission in silver: resolving d and sp contributions in valence band spectra

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Abstract

We present high-resolution valence band and core level spectra of silver for photoelectron kinetic energies up to 8 keV. At these kinetic energies we estimate a surface contribution of less than 3%. Taking advantage of the favourable sp/d relative cross-sections, a comparison with the calculated density of states is presented. We observe an increasing photoemission intensity when approaching the Fermi level, which we assign to a free-electron-like character in the 5p-band, whereas the principal s-like contribution is located at the bottom of the d-band. The difference between measured and calculated values of the sp/d cross-section ratio is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Photoemission spectroscopy (PES) is a versatile, easy-to-use and non-destructive probe of the electronic properties of solids. Low-energy angle-resolved PES (ARPES), in the UV and soft x-ray range, provides detailed information on the electronic states, with a strong surface sensitivity (typically 5–10 Å, corresponding to a few atomic layers) which is especially valuable in surface studies. At higher photon energies, for photoelectron kinetic energies $KE > 500$ eV,

one is in the so-called x-ray photoelectron spectroscopy (XPS) regime: the probing depth of PES increases and results are usually interpreted in terms of partial density of states (DOS), weighted by angular-momentum-dependent transition matrix elements. In fact, even those experiments that one considers bulk sensitive (e.g., using a $h\nu = 1486.6$ eV Al $K\alpha$ source) probe at most 20 Å below the surface [1]: a larger probing depth would be highly desirable in many experiments, with the aim of measuring the truly *bulk* electronic structure of solids. Available model calculations [2, 3] and experimental estimates [4] suggest that an information depth of 40–100 Å can be reached by analysing photoelectrons with KE in the 6–10 keV range.

The extension of PES towards high photon energies offers an additional advantage, namely the controlled modulation of the relative contributions of states with different angular momenta. The use of synchrotron radiation (SR), thanks to its energy tunability, allows one to selectively enhance or depress the photoionization cross-section of a specific element, or of a specific electronic level for a given element. In the case of transition metals, low-KE valence band spectra are dominated by the contribution from states of d symmetry (in silver, for instance, the d/s cross-section ratio is more than 200 for KE between 10 and 300 eV). As a consequence, information on extended states of sp character, relevant to the definition and understanding of the electronic properties of these metals, is hidden. This situation is reversed at high KE: tabulated partial cross-sections of 8 keV photons in Fe, for instance, indicate that the cross-section of the 4s electrons is 10 times larger than that for the 3d electrons [5, 6].

In noble metals, the essential features of the occupied DOS are well known. Nonetheless, it remains difficult to identify the weak signal from the free-electron-like sp-bands in the presence of the strong intensity due to the spatially localized d-states. This leaves open questions, such as (i) establishing the surface versus bulk electron transfer in the valence band across the 3d and 4d series [7] and (ii) giving a theoretical description of the quasiparticle excitations and of their lifetimes. In the latter case, calculations show that, from Nb to Ag, the localization of the d-states increases and, at the same time, their hybridization with the p-states decreases. Also, calculations predict that the free-electron-like character of the p-band is maximum for Ag [8]. On these questions, hard x-ray PES (HAXPES) offers a more detailed insight, complementary to conventional XPS.

HAXPES experiments are difficult from a technical point of view, and very weak signals are expected due to the rapid decrease of the photoionization cross section with energy ($\sim E^{-3}$). These difficulties were illustrated by the pioneering experiments performed in the 1970s [9]. Today, thanks to the development of high-flux/high-resolution beamlines at third-generation SR sources and to recent advances in analyser technology, HAXPES is becoming a viable alternative to standard XPS. Attempts have been made recently to measure core level [4, 10, 11] and valence band [12–15] spectra using hard x-rays. The next step is to bring the energy resolution of HAXPES to values (50–100 meV) comparable to those of low-energy PES, in order to attain a bulk-sensitive description of the partial DOS together with a detailed picture of the low-energy excitations in solids.

In this paper we present high-resolution core level and valence band HAXPES spectra from polycrystalline Ag measured at KE between 6 and 8 keV. The interest of these measurements is twofold: (i) compare HAXPES results to standard XPS spectra and to state-of-the-art bulk-DOS calculations using a well known reference material such as silver, and (ii) look from a new point of view at the problem of identifying and separating the 4d and sp contributions in valence band PES. The weak surface contribution to our spectra permits a simple and reliable comparison with the calculated bulk DOS. Under these conditions, and thanks to the favourable 4d/5sp cross-section ratio, we attempt to identify better and disentangle the s, p and d contributions to the valence band photoemission spectrum of Ag. We compare our experimental values of the sp/d cross-section ratio to available atomic calculations.

2. Experimental details and model calculations

Experiments were performed using the VOLPE (VOLume PhotoEmission) spectrometer, now operational at beamline ID16 of the European Synchrotron Radiation Facility (ESRF, Grenoble). The spectrometer consists of a 200 mm radius hemispherical analyser, with transmission lens, electronics and detector system specifically designed and optimized for the purpose of high-KE experiments [16]⁸. The ID16 undulator beamline was equipped with a Si(nnn) channel-cut monochromator ($n = 3, 4$) working close to backscattering condition (88°). It delivered 6×10^{11} photons/s/200 mA at 5934 eV ($n = 3$) and 8×10^{11} photons/s/200 mA at 7912 eV ($n = 4$), in a bandwidth of 50 and 37 meV, respectively. The spot size at the sample position was 0.05 mm (vertical) \times 0.12 mm (horizontal). The best overall energy resolution (photons + analyser) that we obtained was ~ 70 meV (at 5934 eV) [16]. In order to reduce the acquisition time, data were routinely collected with an energy resolution of ~ 100 and ~ 150 meV, respectively, for valence band and core level spectra. Experiments were performed on a polycrystalline Ag sample, in a base pressure of 4×10^{-8} mbar. After an initial mild Ar⁺ sputtering, no evidence of contamination was found over the entire duration of the experiment, and no further cleaning was required.

To calculate partial DOSs we solved the density-functional theory (DFT) equations using the WIEN2k [17] implementation of the Full Potential Linear Augmented Plane Wave (FLAPW) method, including the generalized gradient approximation (GGA) for the exchange and correlation [18]. We used the tetrahedron method for the calculation of the density of states and of the Fermi energy, and treated spin-orbit interactions in second variation [17]. To simulate the Ag(100) surface, we constructed a seven-layer slab with a vacuum layer which corresponds to the thickness of seven interlayer distances. We adopted the optimized lattice constant of Ag ($a = 4.09$ Å), obtaining full convergence with 4735 k -points and 105 k -points in the irreducible Brillouin zones of bulk and slab calculation, respectively. The energy cutoff was 17 Ryd and the muffin-tin sphere radii were 1.16 and 1.3 Å.

3. Results

In figure 1 we present Ag 3d core level PE spectra measured at $h\nu = 5934$ eV (left panel). The experimental binding energies of the 3d_{5/2} and 3d_{3/2} spin-orbit partners (368.4 and 374.4 eV) and the separation between the main peaks and the bulk plasmon satellites (3.76 eV) agree with published data [19, 20]. In the right panel, a zoom view of the Ag 3d_{5/2} peak obtained at $h\nu = 7912$ eV is shown, along with the values of best-fitting parameters. The fit with a Donjac-Sunjic lineshape [21] with intrinsic width Γ and asymmetry parameter α , plus a Gaussian broadening Σ to account for experimental resolution, yielded $\Gamma(\text{FWHM}) = 240 \pm 20$ meV, $\alpha = 0.05 \pm 0.01$ and $\Sigma(\text{FWHM}) = 170 \pm 20$ meV. Γ and α values agree with previous high-resolution XPS results on polycrystalline Ag samples [19, 22, 23]. In order to quantify the surface contribution, we measured, as in [22], the dependence of the 3d line shape on the take-off angle and fitted the Ag 3d_{5/2} peak with a bulk + surface doublet. Forcing the binding energy of the surface component to be 0.08 eV higher than the main line [22], its intensity is at most 3% of the total. If the binding energy of the surface component is allowed to vary, fitting yields unphysical values for the corresponding peak.

Let us consider now valence band partial cross sections. Ag valence band spectra are shown in figure 2 (left panel), for different photon energies: $h\nu = 25$ eV (UPS regime), $h\nu = 1486.6$ eV (XPS) and $h\nu = 7912$ eV (HAXPES). The narrower d-band contribution

⁸ The dispersive element is from MBScientific AB, Sweden (www.mbscientific.se).

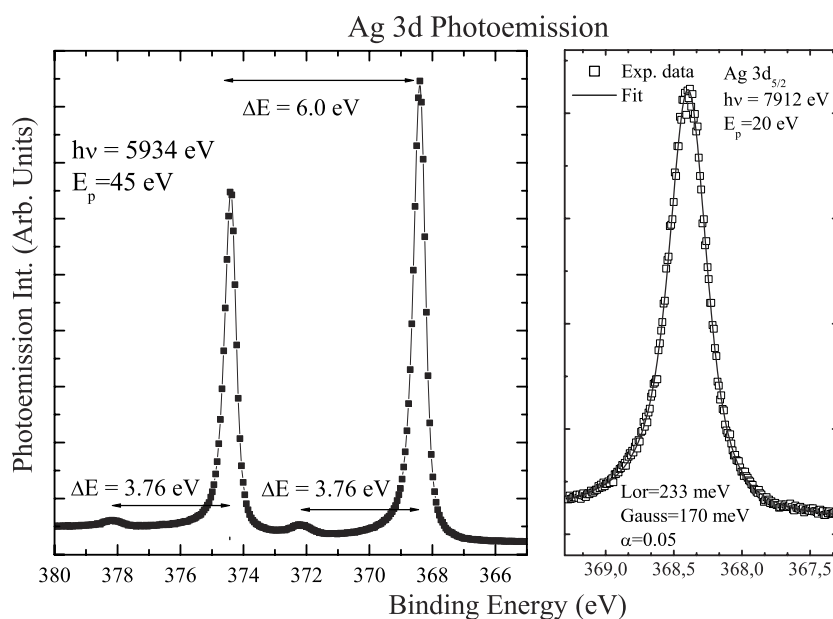


Figure 1. Left: Ag 3d core level spectra measured at $h\nu = 5934$ eV and pass energy $E_p = 45$ eV. The acquisition time was one hour. For each spin-orbit partner a bulk plasmon satellite is visible, with indicated values of the relative energy separation. Right: the $3d_{5/2}$ peak (open squares), as measured at $h\nu = 7912$ eV and $E_p = 20$ eV, with the result of the fit obtained after subtraction of an integral (Shirley) background. An asymmetric Donjac-Sunjic lineshape was used, broadened by a Gaussian to account for experimental resolution. The resulting Lorentzian intrinsic width Γ , Gaussian broadening Σ , and asymmetry parameter α are indicated.

in UPS is due to its strong surface sensitivity. Another feature that distinguishes the UPS spectrum is the steady decrease of the photoemission intensity when the binding energy (BE) approaches the Fermi level (E_F). This confirms that the d contribution dominates, its tail hiding the signal from states of different symmetry.

The right panel of figure 2 compares the XPS and HAXPES spectra, rescaled to a common integrated intensity of the d-band. Although the two spectra are rather similar, a close look at the Fermi edge region reveals that the HAXPES spectrum ($h\nu = 7912$ eV) exhibits an increasing intensity towards E_F , a feature that was predicted by model calculations [19, 23], but never observed so far.

Figure 3 compares HAXPES spectra ($h\nu = 5934$ eV and 7912 eV) to DOS calculations (both surface and bulk). Looking at the two experimental spectra (normalized to the maximum intensity at the bottom of the d-band), one notices that the intensity increase towards E_F is more pronounced at 7912 eV than at 5934 eV. The calculated bulk electron density at E_F (~ 0.25 states/eV) agrees well with previous reports [24] and the width of the d-band (3.4 eV) is consistent with available XPS data [25]. HAXPES spectra and bulk DOS calculations match very well in the d-band region. The five components that can be clearly identified in both calculation and experiment are due to the crystal-field split Ag 4d orbitals: the first, third and fifth peaks correspond to t_{2g} symmetry and the two others to the e_g symmetry. The relative intensities of these components depend strongly on the details of the calculation [24, 25]. Both the general shape of the d-band and the relative intensities of the peaks strongly differ from surface DOS calculations [27], which rather match the UPS spectrum of figure 2.

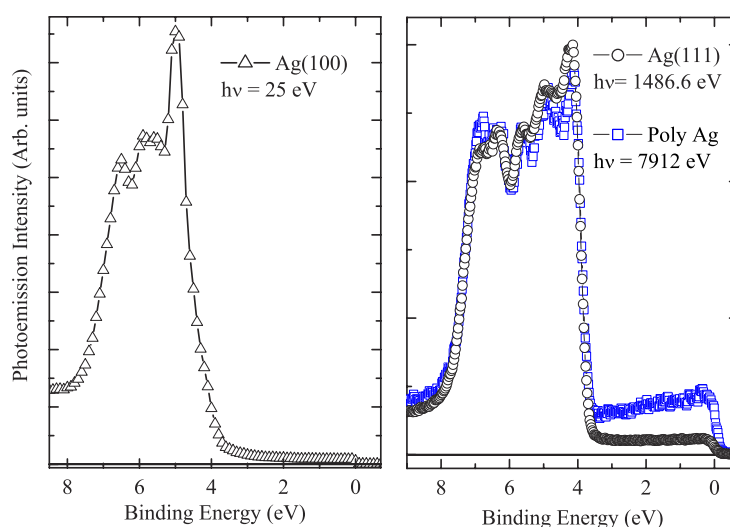


Figure 2. Left panel Ag(100) valence band spectra measured at $h\nu = 25$ eV. Right panel. Valence band spectra measured with Al $K\alpha$ line at $h\nu = 1486.6$ eV (Ag (111), open circles) and $h\nu = 7912$ eV (polycrystalline Ag, open squares). Spectra have been rescaled to have equal intensities of the d-band.

The erroneous position of the top of the d-band with respect to E_F in the bulk DOS (2.7 eV against an experimental value of 3.7 eV) is a typical feature of this kind of calculation in noble metals [24–26]. Two possible explanations have been suggested: one attributes this discrepancy to the inability to write the exact exchange and correlation potentials, the other ascribes it to the fundamental difference between the DFT approach (describing ground state properties) and PES, probing single-particle excitations which incorporate self-energy corrections. Recent calculations for Cu show that the discrepancies between PES and DFT results are almost completely corrected by including self-energy effects [28, 29].

4. Discussion

Having ascertained that the surface contribution is negligible at $KE \geq 6$ keV, we compare our experimental results to the bulk DOS calculations only. Table 1 summarizes, for the photon energies of interest here, the calculated values of the d and s atomic cross-sections of silver⁹, according to Yeh and Lindau [5] and Scofield [6]. Although the 8 keV values differ considerably from one calculation to the other, the ratio between the cross-sections of d to s levels are very close (~ 7 in both cases). The d/s ratio is reduced by roughly one order of magnitude going from the UPS to the XPS photon energies, then by another order of magnitude when moving to the HAXPES regime.

In figure 4 we compare the calculated partial s, p and d DOSs with the experimental valence band measured at $h\nu = 1486.6$ eV and $h\nu = 7912$ eV (panels (a), (b), respectively). No additional broadening has been used in calculated DOS¹⁰. For each energy, we constructed

⁹ Being atomic calculations, they do not consider the 5p electrons for silver.

¹⁰ Consistently with [19], the best agreement with the experimental d-band is obtained by applying to the calculated DOS a Lorentzian broadening that increases from 0.2 to 0.5 eV, following a quadratic behaviour with the binding energy of the d-states. Such a behaviour is expected when the excitation energy is large enough to excite all d electrons [30].

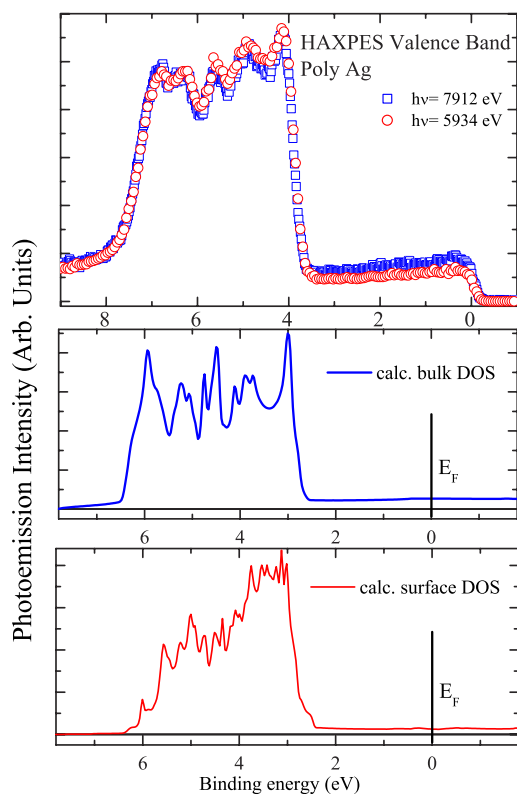


Figure 3. Top panel: valence band spectra of Ag measured at $h\nu = 5934$ eV (red circles) and 7912 eV (black squares). Central panel: calculated total bulk DOS. Bottom panel: calculated total surface DOS. Calculated curves have been arbitrarily shifted on the horizontal scale to match the experimental d-band position. The vertical black bars labelled E_F indicate the theoretical position of the Fermi level (see text for the discussion). The horizontal black line indicates the baseline of the calculation.

Table 1. Calculated Ag 4d and 5s cross-sections at selected photon energies, from [5] and [6]. The values from [5], labelled 8 keV for simplicity, correspond to the tabulated values at 8047.8 eV. Values are in Mbarns/shell, i.e. taking into account the total occupation number per shell.

	Ag cross-section at selected photon energies (Mbarns/shell)					
	25 eV	1486 eV		6 keV	8 keV	
Ag 4d	16.62 ^a	2.10×10^{-2} ^a	2.05×10^{-2} ^b	2.4×10^{-5} ^b	0.9×10^{-4} ^a	4.2×10^{-6} ^b
Ag 5s	0.03 ^a	2.90×10^{-4} ^a	2.87×10^{-4} ^b	3.84×10^{-6} ^b	1.3×10^{-5} ^a	5.82×10^{-6} ^b
Ratio 4d/5s	554	72.4	71.4	6.3	6.9	7.2

^a From Yeh and Lindau [5].

^b From Scofield [6].

a fitting curve by optimizing the weight of the s, p and d DOS contributions (full lines in figure 4). At 7912 eV, the best fit is obtained with the ratio of the integrated intensities $I(4d)/(I(5s)+I(5p)) = 1.55 \pm 0.15$. At 1486.6 eV, the ratio increases to ~ 40 . Corresponding expected values are ~ 7 and ~ 70 , respectively. A few additional remarks about this data analysis are worth making.

Knowing that PES is a probe of filled states only, it may be more appropriate to integrate the intensity up to the experimental value of E_F , considering only the filled states. In this way,

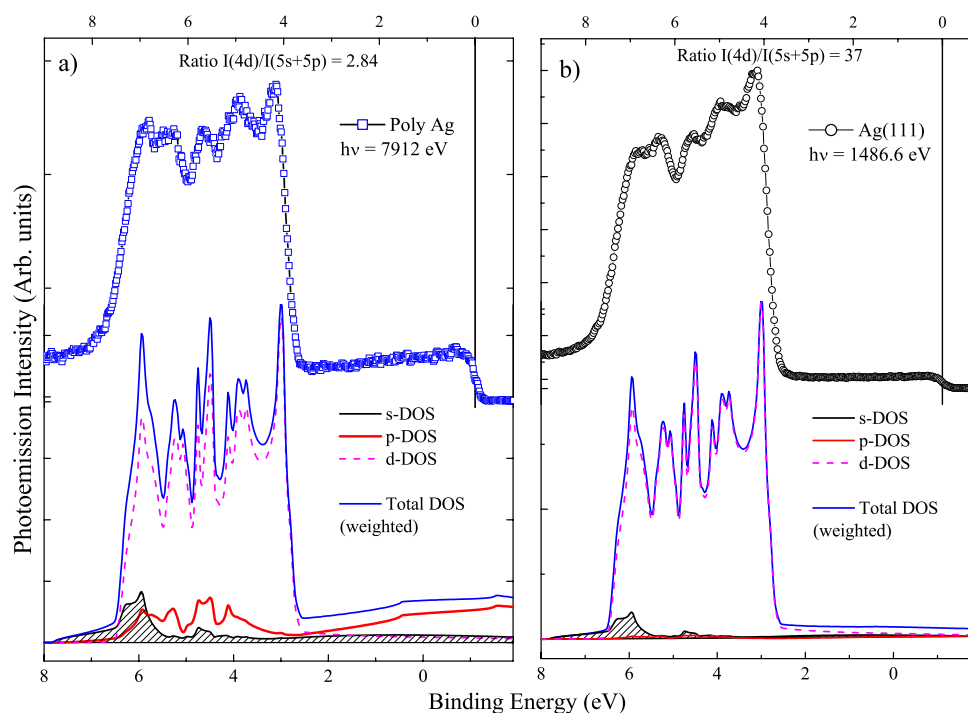


Figure 4. Valence band spectra measured at $h\nu = 7912$ eV on polycrystalline Ag (open squares) and with Al $K\alpha$ $h\nu = 1486.6$ eV on Ag(111) (open circles), compared to the total weighted DOS (blue line); the weighting has been obtained by multiplying partial s, p, d DOSs. The vertical line indicates the Fermi levels of the experimental spectra, and the horizontal lines indicates the baseline of the calculated partial DOS, with s (black line with shaded area), p (red line) and d (violet dashed line) DOS. The bottom and top x -axis indicate, respectively, the energy scale for calculation and experiment. Calculated DOSs have been arbitrarily shifted for comparison.

one obtains a ratio $I(4d)/(I(5s) + I(5p))$ of 3.8 ± 0.1 at $h\nu = 5934$ eV and of 2.8 ± 0.1 at $h\nu = 7912$ eV. This latter value, although larger than the previous estimate, is still a factor of 2 smaller than the tabulated atomic d/s ratio.

Alternatively, we also modelled the HAXPES spectrum near the Fermi level by a free-electron-like parabolic band, after an integral background subtraction. The parabolic band had its starting point at the bottom of the d-band, i.e. where the calculated s-DOS has its maximum intensity: also in this case the ratio of the integrated intensities $I(4d)/I(5s)$ is smaller than 3.

Turning to the XPS spectrum, the main contribution arises from the d-band, with an s intensity higher than the p one. However, the almost flat intensity above the d-band makes the separation of the s, p and d contributions more difficult than in HAXPES, where the increasing intensity near the Fermi level can be used as a marker to distinguish between s and p DOSs.

Our analysis of the experimental HAXPES and of the calculated spectra suggests that the increasing intensity towards E_F is associated mostly to the p-level contribution. This result supports the picture predicted in [7] of a free-electron-like band of silver of mostly 5p character.

Although the d-band is located well below E_F , the contribution of the d-levels to the total DOS extends up to the Fermi level. Jepsen *et al* [31] already pointed out that this should imply a significant fraction of d-holes per atom due to sp-d hybridization. Moreover, s-states are located at the bottom of the d-band, revealing a more localized character with respect to the

p ones [7]. This is confirmed in figure 4 by the high binding energy tail in the spectrum at around 7.5–8 eV, clearly of s character.

To some extent, the comparable intensities of the first (~ 7 eV) and fifth (~ 3 eV) peak of the experimental d-band also reveal the presence of the s contribution around 8 eV of binding energy. This is not the case for the XPS spectrum, which displays an overall d-like lineshape, with an increasing intensity from the first to the fifth peak of the d-band.

5. Conclusions

The 3d and valence band HAXPES spectra of polycrystalline Ag display larger bulk sensitivity and improved energy resolution with respect to standard XPS. Already at 6 keV of kinetic energy the surface signal is negligibly small, indicating a maximum surface contribution of less than 3%. These findings give a firm experimental basis for a direct comparison of HAXPES valence band spectra to calculated bulk DOS, without any further assumption about the surface contribution. By optimizing the weight of the calculated s, p and d DOSs in order to match valence band spectra measured at different photon energies, we found a reduced $I(4d)/(I(5s) + I(5p))$ ratio with respect to calculated values, namely ~ 40 instead of ~ 70 in the XPS regime and 2.8 instead of 7 at $h\nu = 7912$ eV.

Taking advantage of the favourable 4d/sp cross-section ratio, HAXPES spectra yield a more accurate picture of the Ag valence band. The comparison between experiment and calculation reveals that the 5p-band is responsible for the observed increase of the intensity when approaching the Fermi level and has the strongest free-electron-like character, whereas localized s-states are present at the bottom of the d-band.

Our results, obtained for a reference system like Ag, set the basis for extending this technique to other materials. Comparing DOS calculations to HAXPES data and exploiting the behaviour of photoelectron cross-sections at high kinetic energy will make it possible to have a new point of view to look at the electronic properties of complex systems like, for instance, transition metal oxides. Finally, in spite of the more challenging experimental conditions of HAXPES with respect to XPS, we anticipate potential applications to the study of samples of technological interest, thanks to the more relaxed vacuum and surface preparation requirements.

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