PHYSICAL REVIEW B VOLUME 14, NUMBER 6 15 SEPTEMBER 1976

High-resolution x-ray photoemission spectra of silver

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(Received 18 November 1975)

An electron spectrometer fitted with an x-ray monochromator for Al $K\alpha_{1,2}$ radiation (1486.6 eV) has been used to record high-resolution x-ray photoelectron spectra for the $4d$ valence band as well as the $3d$ spin doublet in silver. The core-level spectrum has a line shape that can be described successfully in terms of the many-body theory of Mahan, Nozières, and De Dominicis. The $4d$ spectrum agrees well with predictions based on a relativistic–augmented-plane-wave band-structure calculation.

I. INTRODUCTION

In the past decade, photoemission spectroscopy has become established as a powerful tool for investigations into the electronic structure of solids. The results show a dependence upon the energy of the incident photon and for convenience the technique is subdivided into two areas, based on ease of experimental accessibility: ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS).

Although the two branches of the technique are complementary (for orbital-symmetry identification), each has its own particular advantages and disadvantages. UPS offers higher photoionization cross sections and higher-resolution analysis (0.2–0.4 eV), but is restricted in its energy range to valence bands. Its main disadvantage here is that the low energy results in a spectrum which reflects the joint density of states. XPS provides spectra with a lower background, enables core levels to be studied in addition to valence bands and, because the unoccupied density of states at 1 keV or more above the Fermi energy has no significant structure, enables the occupied density of states to be determined directly. The main disadvantage of XPS has been poor energy resolution. Initially characteristic Mg $K\alpha$ radiation was used, giving a resolution of 0.8 eV. Later developments over the past few years involving monochromatization of the Al $K\alpha_{1,2}$ line have succeeded in closing the gap so that XPS may now be carried out at a resolution of better than 0.4 eV.

The work presented here involves such a high-resolution XPS investigation for silver. High resolution offers an opportunity to make meaningful comparisons of experimental and theoretical line shapes for both core levels and valence bands. For core-level studies, a higher-resolution spectrum provides a more accurate approximation to the natural line shape thus facilitating analysis with a theoretical many-body line-shape function such as that of Doniach and Šunjić.[1] We have made such an analysis for the Ag $3d$ spin doublet and find that the theoretical line shape fits the experimental one extremely well after folding with the instrumental resolution function. When we adopt a similar approach for the Ag $4d$ band, we find that a reasonably good fit can be obtained if we allow the lifetime width to vary across the band when folding the density-of-states function with the Doniach-Šunjić function.

II. EXPERIMENTAL

The apparatus used was an AEI ES200 electron spectrometer, fitted with an x-ray monochromator for Al $K\alpha_{1,2}$ radiation (1486.6 eV), a non-monochromatized Mg $K\alpha$ source (1253.6 eV), and an ion gun for sputter cleaning. The instrument has been described elsewhere.[2]

Photoemission spectra were recorded with the monochromatized x-ray beam incident at 40° to the surface while the ejected photoelectrons were detected at 90° to the surface.

A polycrystalline silver sample was used and cleaning was effected by heating to 300 °C followed by argon-ion bombardment until wide-scan XPS spectra, taken with the standard Mg $K\alpha$ source, showed the virtual absence of common contaminants. XPS spectra using the monochromatized source were then recorded at room temperature. The sample chamber pressure remained below 10^{-9} Torr during measurements.

The electron energy analyzer was operated in the fixed-retarding-ratio mode in which $\Delta E/E$ is constant. For the $3d$ spectrum the analyzer contribution to the energy spread was estimated as $\Delta E_a = 0.11$ eV (full width at half-maximum, FWHM) and for the valence-band region it was 0.18 eV. The overall instrumental contribution as determined from the derivative of the Fermi

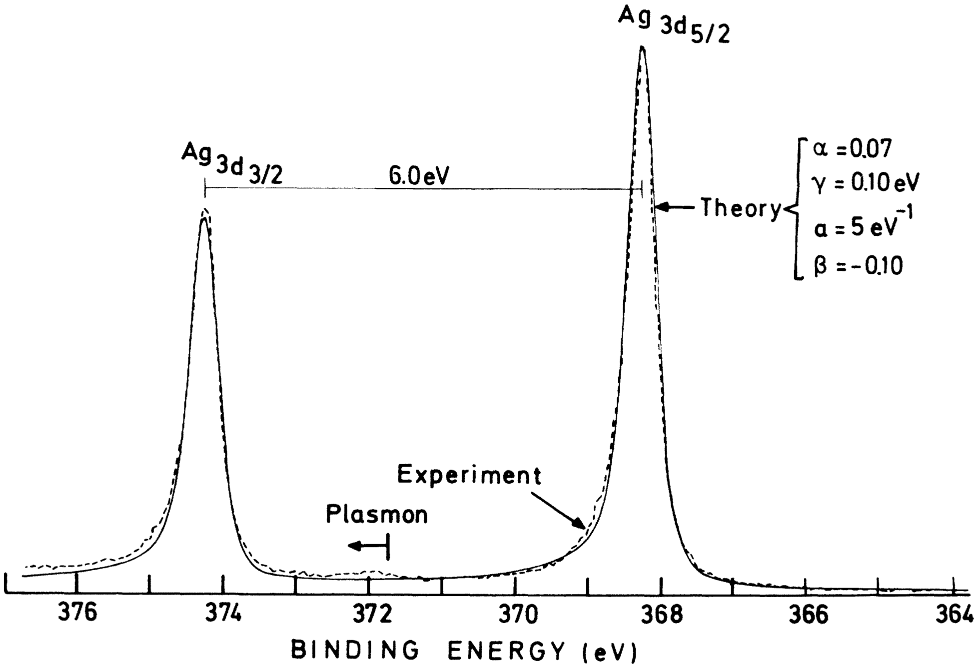

FIG. 1. X-ray photoemission spectrum from the $3d$ core levels in solid silver. The broken curve represents the experimental results, whereas the full line is obtained from the theoretical line-shape function [Eq. (1) and Eq. (2)]. The theoretical curve was scaled in amplitude to the experimental at the $3d_{5/2}$ peak, and the $3d_{3/2}$ amplitude was taken as $\frac{2}{3}$ of the $3d_{5/2}$ value.

edge was 0.38 eV. Spectra were obtained by step scanning the analyzer and storing counts in a multichannel analyzer using steps of 0.05 eV with a dwell time of 0.8 sec per channel. A sufficiently large number of scans were stored to achieve an acceptable signal-to-noise ratio.

III. RESULTS AND DISCUSSION

A. Ag 3*d* core levels

According to Siegbahn[3] the experimental values of the x-ray levels corresponding to the $3d$ states in silver are -379.6 eV ($3d_{3/2}$) and -374.1 eV (± 0.7 eV) ($3d_{5/2}$). These results cannot be directly related to the binding energies of the $3d$ electrons in the free atom because of ambiguity in reference levels, and because the charge compression in the solid will change the energies even of such low-lying core states. Therefore, a calculation of the one-electron eigenvalues for a free atom should not agree with these values. Further, conventional Hartree-Fock-Slater (HFS) or $X\alpha$ atomic calculations should rather[4] be replaced by similar schemes using fractional occupation numbers when applied to calculate optical transition energies for electrons excited from strongly localized states. It is therefore not surprising that the energy levels obtained by Herman and Skillman,[5] $E_{d_{3/2}} = -393.9$ eV, $E_{d_{5/2}} = -387.3$ eV, differ from the experimental energy levels. These atomic levels were obtained from self-consistent nonrelativistic HFS calculations, but corrected to include the relativistic shifts and the spin-orbit splitting. If the fully relativistic Dirac-Slater calculation is carried through to self-consistency we obtain energy values that are considerably closer to the experimental binding energies, namely, -382.14 and -375.62 eV. Both types of atomic calculations included the Slater exchange with its full weight. The latter, fully relativistic calculation, is the one that was used to produce the atomic potential applied in the construction of the muffin-tin potential for the band-structure calculation.[6]

The spin-orbit splitting as calculated for the $3d$ atomic levels is 6.5 eV, which, in view of the estimated uncertainties in the experimental values of Ref. 3, in not in disagreement with this experiment.

We calculated the $3d$ energy eigenvalues in the solid using the *muffin-tin potential* (the same as applied in the band-structure calculation[6]). Using the Fermi level as a reference, these energy levels are $E_{d_{3/2}} = -375.50$ eV and $E_{d_{5/2}} = -368.97$ eV. Figure 1 shows the XPS spectrum for the $3d$ core levels, and it follows that the experimental binding energies, 374.3 and 368.3 eV, are quite close to the calculated values, although the theoretical estimate of the binding energies in the crystal, just as the atomic calculation, does not take localization effects into account. The experimental value of the spin-orbit splitting is 6.0 eV, i.e., 0.5 eV smaller than the calculated value. This discrepancy cannot be explained in terms of the experimental uncertainty since this is smaller than 0.1 eV.

If the work function of silver (4.2 eV) is added to the Dirac-Slater values a comparison with the energy levels calculated for the crystal potential gives an estimate of the shifts due to the charge compression in the solid. Both 3*d* levels appear to be shifted upwards in energy by 2.4 eV when the solid is formed.

The resolution of the spectrometer used in the present experiment is so good that a test of the Mahan–Nozières–De Dominicis theory[7,8] may be possible by comparing theoretical and experimental line shapes.

Similar work has been presented recently by Hüfner and Wertheim,[9] who demonstrated that the shapes of a large number of XPS spectra could be described in terms of the line-shape function derived by Doniach and Šunjić.[1] This function is

$$I(\Delta E) \propto \frac{\cos[\pi\alpha/2 + (1-\alpha)\arctan(\Delta E/\gamma)]}{(\Delta E^2 + \gamma^2)^{(1-\alpha)/2}} \quad , \qquad (1)$$

where ΔE is the energy measured from the threshold of the unbroadened line, γ is the lifetime width, and α is an asymmetry parameter related to the partial-wave phase shifts for scattering of electrons at the Fermi level on the "impurity potential" of the deep-lying hole[7,8] or, for transition metals, an empty *d* state created in the neighborhood of E_F.[10,11] In order to be able to reproduce the experimental spectra the line-shape function (1) must be folded by a function that accounts for instrumental broadening. The instrumental resolution function was determined as the derivative of the Fermi edge (see Fig. 4). The derived function was approximated by a skew Gaussian, similar to the one used in Ref. 9:

$$G(\Delta E) \propto e^{-[a\Delta E/(1+a\beta\Delta E)]^2} \quad , \qquad (2)$$

in which $a = 5.0\ \text{eV}^{-1}$ and $\beta = -0.10$.

The experimental XPS trace is shown in Fig. 1 together with the best calculated spectrum. A large number of parameters α and γ have been used for calculations of the line shapes, but only one set seems to be able to reproduce the observed shapes. The best values of α and γ are 0.07 and 0.10 eV, respectively, and judging from the large amount of trial calculations, the uncertainties in α and γ are estimated to be ±0.01 and 0.01 eV, respectively. After having determined a reasonable range of values of α and γ, we tried to vary a and β, the parameters in the instrumental resolution function, but ended up with the values estimated as described above. The value of α which we have determined agrees well with the results obtained by Wertheim and Hüfner,[9,11] who quote $\alpha \approx 0.05$ for Ag and Au. The experimental trace has not been modified by any means, not even a background function has been subtracted. It follows that the line-shape function (1) with the present choice of the parameters fits the experiment extremely well, the only essential discrepancy being due to the plasmon.

B. 4*d* band of silver

The XPS spectrum of the 4*d* states will be compared to theoretical predictions based on a relativistic–augmented-plane-wave (RAPW) band-structure calculation presented earlier.[6] It has been demonstrated[6] that this calculation places the top of the 4*d* band at the correct energy when compared to optical experiments, the main interband edge being 3.98 eV. Also the width of the *d* band agreed well with photoemission experiments except for minor discrepancies at the band bottom. These disagreements do not, however, unambiguously demonstrate errors in the band structure; they may be explained in terms of asymmetry in the photoemission line shapes. It was, however, realized[6] that the *s*-*d* admixture at the Fermi level appears to be too weak since the anisotropy of the calculated Fermi surface was too small when compared to experiments. An increased *s*-*d* admixture may also increase the value of the *L* gap ($L_4^- \rightarrow L_4^+$) which, although in agreement with some interpretations of optical experiments,[12] is too low when compared to other experiments.[13] In spite of the difficulties mentioned the calculation of Ref. 6 will be used in the present work since we essentially need only the density-of-states function in the 4*d*-band regime.

Roughly, the x-ray photoemission experiment referring to initial states 0 to 9 eV below E_F in silver will reflect the density-of-states function (DOS). This function has been derived from the RAPW band-structure calculation and is shown in Fig. 2. In the same figure is also shown the experimental XPS trace. The figure shows that there are notorious differences between the two curves although the main peaks can be correlated. The line shape of the experimental spectrum differs significantly from the DOS, but also some of the calculated spectral positions of the peaks are off. The fact that the peak positions do not agree can be attributed to the band calculation itself. It appears that the low-lying *d* states should be moved somewhat downwards. The discrepancy may also be ascribed to the fact that we are try-

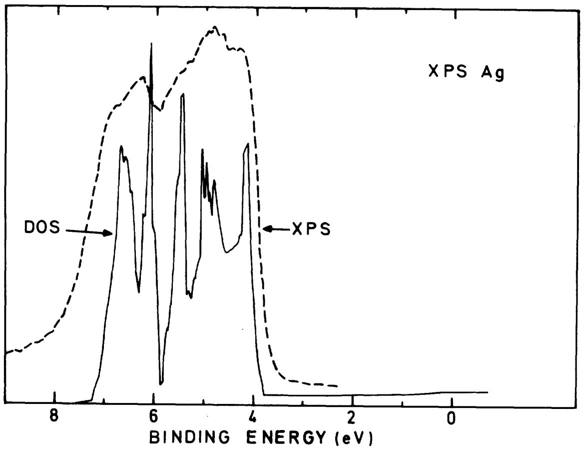

FIG. 2. Density-of-states function for silver (full line, DOS) derived from the RAPW band-structure calculation (Ref. 6). The broken curve is the experimental XPS spectrum.

ing to compare ground-state energies to the experiment, in which, in fact, excited states are studied. A sort of renormalization can be introduced in the theoretical spectrum in order to allow a comparison. A crude model that introduces such shifts has been used by Moruzzi *et al.*[14] However, their correction does not seem to be theoretically justified for application to the silver *d* band and therefore we decide not to use it here. The *d* states are localized at the top of the band, whereas the low-lying *d* states are rather extended. Therefore, if we were to introduce shifts in the band structure, a model that produces larger shifts at the top of the *d* band than at the bottom would seem more reasonable.

One of the most striking differences between the line shapes of the calculated DOS and the XPS spectrum is that the elements of structure in the DOS are much sharper than in the experimental trace. A simple folding of the DOS with a Lorentzian can to some extent simulate the lifetime broadening and the broadening due to a finite instrumental resolution. Figure 3(a) shows the DOS after such a broadening (broken curve) with a Lorentzian of 0.4-eV FWHM. It appears, however, that there is at most only a fair agreement between the theoretical and experimental line shapes. It is characteristic that the amplitudes of the experimental peaks are considerably larger at top (E_A) of the *d* band than they are at the bottom (E_B), whereas the theoretical amplitudes are almost the same near E_A and E_B. This fact has been ascribed to differences in the optical transition matrix elements, but as shown below it can also be ascribed to a lifetime broadening that varies across the *d* band.

Although the validity of the theory from which the line-shape function (1) was derived may be questioned when applied to the 4*d*-band states we have tried to use (1) also in this energy regime. *A priori*, one should not expect the same asymmetry index α (0.07) as was used for the core levels to be the optimum value for the 4*d* spectrum as well. Further, since this spectrum in contrast to core-level spectra covers a wide energy range over which the localization effects may vary, we cannot expect that the same set of parameters can be used throughout the spectrum. Roughly, we would expect that excitation of a strongly localized

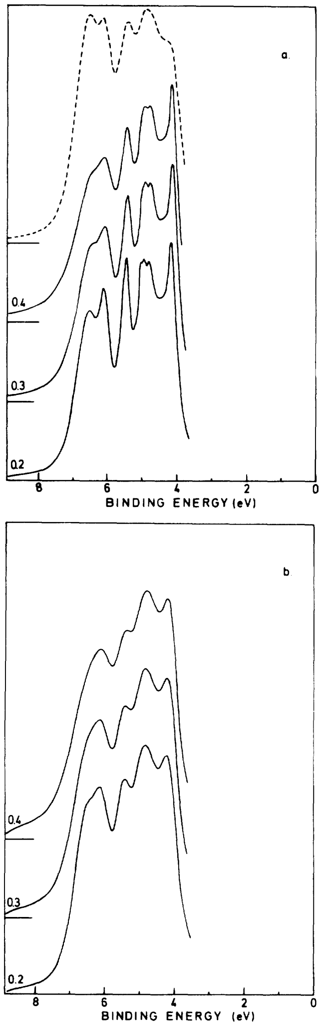

FIG. 3. (a) Theoretical line-shape functions derived by folding the RAPW DOS with the Doniach-Šunjić function [Eq. (1)] but including a γ that varies over the *d*-band range. The numbers indicate the γ value (in eV) at the bottom of the *d* band. The broken curve is the DOS function after a simple Lorentz folding (0.4-eV FWHM). (b) The theoretical curves of (a) after convolution with the instrumental line function [Eq. (2)].

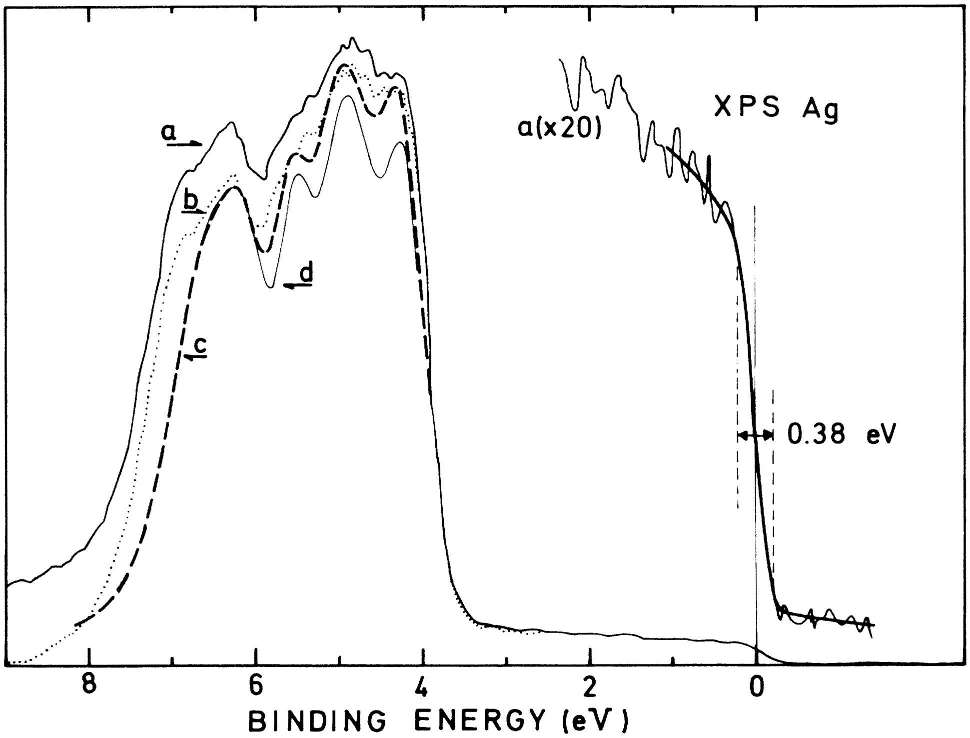

FIG. 4. Curve a is the experimental $4d$ XPS spectrum of silver, whereas b was obtained by subtracting a smooth background function. The curve marked c is the theoretical spectrum including the Doniach-Šunjić line-shape function with a lifetime width γ that varies across the d band. The maximum value of γ is 0.3 eV at the bottom of the d band. The asymmetry parameter α is 0.07. Curve d is a similar calculation with $\alpha = 0$, i.e., a simple Lorentz line-shape function with a varying γ.

d electron (near the top of the *d* band) would produce a strongly localized hole, implying that γ should be small at the top of the *d* band and larger at the bottom. In the present model γ is assumed to increase quadratically with the energy measured from the top of the *d* band. The theoretical line shape is calculated by folding the density-of-states function by the function (1), where γ varies in the manner described. Again, this must further be folded by the instrumental line-shape function in order to be compared to the experimental trace. Figure 3(a) shows the calculated spectra (full-line curves) obtained from the modified Doniach-Šunjić function, but before the instrumental broadening has been introduced. The numbers give the maximum value of γ, i.e., the value which is used at the bottom of the *d* band. The spectra in Fig. 3(b) have been obtained after inclusion of the instrumental function. Finally, Fig. 4 shows the best theoretical curve (*c*) together with the experimental traces (*a* and *b*). It appears that the present simple approach is sufficient to reproduce the observed line shape and to yield the correct amplitude ratios. However, the shoulder at high binding energies in the observed spectrum has disappeared in the calculation. The fact that this contribution is missing may be, as mentioned earlier, ascribed to inaccuracies in the band calculation, or to the fact that spectral positions of the elements of structure have not been shifted by (a varying) relaxation energy. In addition, the experimental spectrum may at high energies (binding energy) contain plasmon satellite structure, which is not included in the theoretical model, and *d* band contributions from surface atoms. This latter type of contribution would be expected to appear at lower initial-state energies (higher binding energies) than the bulk band contribution since the total *d*-*d* overlap is reduced near the surface. The Doniach-Šunjić line-shape functions used in the calculations shown in Fig. 3 and curve *c* in Fig. 4 were all evaluated for $\alpha = 0.07$, i.e., the same value as applied in the case of the core levels. Further calculations have shown that, in the present model, a choice of a larger value for α produces a worse fit to the experiment. An increase of α to 0.2 causes the two peaks at the top of the *d*-band to have the same amplitude, which is in contrast to the experiment. On the other hand, a reduction of α to 0, i.e., modifying the line-shape function to a simple Lorentzian line-shape function with γ varying as described above, seems to lead to a slightly poorer agreement with the experiment (see curve *d* in Fig. 4) than was obtained for $\alpha = 0.07$. It has been estimated from a series of calculations that the optimum value of α is in the range ≈ 0.00 to ≈ 0.10, when the present line-shaped model is applied to the 4*d*-band spectrum of silver.

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