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Photoemission spectra and band structures of *d*-band metals. IV. X-ray photoemission spectra and densities of states in Rh, Pd, Ag, Ir, Pt, and Au

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X-ray photoemission spectroscopy (XPS) data for the valence bands of Rh, Pd, Ag, Ir, Pt, and Au are compared with densities of states calculated from interpolated band structures. The parameters of the interpolation scheme were obtained in an earlier paper by fitting first-principles augmented-plane-wave calculations, and then making adjustments, where necessary, to the width of the *d* bands in order to improve agreement with ultraviolet photoemission spectroscopy (UPS) data. In the 4*d* metals, Rh, Pd, and Ag, there is excellent agreement between the energy positions of peaks in the occupied density of states and the XPS valence bands. In the 5*d* metals, Ir, Pt, and Au, the agreement is reasonable, but inferior to that for the 4*d* metals particularly in the middle of the *d*-band region. It is argued that the main discrepancies in peak locations are not significant and are most likely due to the approximations in the interpolated band structures, particularly those involved in the spin-orbit splitting and hybridization. The relative intensity of the XPS data in the lower-energy region of the *d* bands is consistently lower than that in the density of states, indicating appreciable modulation of the spectra by optical-transition strengths.

I. INTRODUCTION

Photoelectron spectroscopy of solids is conducted in two distinct and widely separated frequency ranges. X-ray photoemission spectroscopy (XPS) generally employs Mg or Al $K\alpha$ photons with energies of 1.25 and 1.49 keV, respectively. Ultraviolet photoemission spectroscopy (UPS) is performed in the photon energy range $\hbar\omega < 41$ eV. If the light is admitted to the sample chamber through a LiF window, the frequencies of UPS experiments are still further restricted to the range $\hbar\omega < 12$ eV. Experiments of this latter kind performed on clean and cesiated samples of Rh, Pd, Ag, Ir, Pt, and Ag have been reported in a previous paper of this series[1] (hereafter referred to as II), and it has been shown in another paper[2] (hereafter referred to as III) that the energy locations of structure in the spectra can be understood to a considerable degree on the basis of one-electron band theory. This has permitted the construction of empirical band structures for these metals. In this paper, we present high-resolution XPS data on these metals, and we investigate the extent to which the results can be correlated with the same empirical band structures.

Systematic comparisons between UPS, XPS, and the predictions of band theory of the kind attempted here are of considerable interest. There is some reason to suppose that the apparent band structures "seen" in XPS and UPS might differ from each other. Such a difference could come about through either: (i) a difference in sampling depth between the two experiments, the one with the smaller sampling depth displaying a narrower width for the *d*-bands[3]; or (ii) differences in the role of many-body relaxation effects in the two frequency ranges.[4] If on the other hand, the band structures seen by UPS and XPS are essentially identical, our comparisons should yield information on the variations of the optical-transition strengths across the *d* bands.

Surveys comparing low-resolution XPS data with band theory have been reported by Fadley and Shirley,[5] by Baer *et al.*,[6] and by Poole *et al.*[7] Higher-resolution XPS data have been presented by Kowalczyk *et al.*[8] and by Hüfner and co-workers.[9] The distinguishing feature of the present work is an attempt to make a detailed and systematic comparison between UPS, high-resolution XPS, and the predictions of band theory for several similar metals.

II. UPS, XPS, AND BAND STRUCTURE

A. UPS

According to one-electron band theory, the photoelectron energy spectrum in a UPS experiment is expected to resemble a property of the band structure called the energy distribution of the joint density of states[2,10] (EDJDOS) which is defined by the following integral over the Brillouin zone (BZ):

$$D(E,\hbar\omega)=\sum_{f,i}\int_{\mathrm{BZ}} d^3k\,\delta(E_f-E_i-\hbar\omega)\,\delta(E-E_i)\,. \quad (1)$$

$E_f(\vec{k})$ and $E_i(\vec{k})$ represent the energy eigenvalues at $\vec{k}$ in a final band f and an initial band i, respectively, and $\hbar\omega$ is the photon energy.

The first δ function in Eq. (1) expresses the requirement of $\vec{k}$ conservation in the optical transition and restricts the integral to those points in k space lying on the optical energy surface given by

$$E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega = 0 \ . \tag{2}$$

The summation in (1) is over all pairs (f, i) of bands which can participate. In general, there will be contributions to the EDJDOS from more than one pair of bands and therefore from more than one surface of the type given in Eq. (2). We will return to this point later in connection with XPS.

B. XPS

In XPS studies of valence bands, it is customary to compare experimental spectra with the ordinary density of states (DOS) defined by:

$$\rho(E) = \sum_i \int_{\mathrm{BZ}} d^3k \, \delta(E - E_i) \ . \tag{3}$$

The justification for using the DOS rather than the EDJDOS is readily seen as follows. In the region of 1 keV above E_F, it is anticipated that there will be very many bands and therefore very many surfaces of the kind defined by Eq. (2). These surfaces will be distributed densely, and more or less uniformly, throughout the BZ. In this situation, the sampling of k space represented by Eq. (1) will tend to become indistinguishable from that represented by Eq. (3).

There are other possible effects which will reinforce this expected resemblance between the XPS spectrum and the DOS. For example, many-body relaxation effects[4] in the optical transition will tend to remove the requirement of strict one-electron $\vec{k}$ conservation embodied in Eq. (1). The surfaces defined by Eq. (2) will then not be sharp, but will be smeared out in k space. Also the wave vector of an x-ray photon is appreciable in comparison with the dimensions of the BZ. This will also weaken the $\vec{k}$ conservation requirement. Note, however, that these additional effects are not essential to our assertion; the XPS spectrum is expected to resemble the DOS even in a direct-transition one-electron model. Qualitatively, we expect that, at low photon energies, the profile of the photoelectron energy spectrum will fluctuate considerably when $\hbar\omega$ is varied. This is because the surfaces represented by Eq. (2) move through k space, so we sample a continually changing section of the energy-band structure. As $\hbar\omega$ is increased, however, more and more surfaces are introduced, so we expect the fluctuations to die away and the spectrum to stabilize at something resembling the DOS. Recent experiments by Eastman and co-workers,[11] using synchrotron radiation, indicate that such stabilization occurs at photon energies as low as 30 eV.

Important factors which have been omitted are the momentum matrix elements. It has been assumed above that each optical transition contributes with equal weight. Each transition should, however, be weighted with the square of a momentum matrix element. One of the hopes of the present work was that variations of the momentum matrix elements would reveal themselves as discrepancies between the calculated DOS and the XPS spectrum.

C. Numerical results for the density of states

Model band structures for Rh, Pd, Ag, Ir, Pt, and Au have been described in III. These were obtained by fitting a combined interpolation scheme to first-principles augmented-plane-wave (APW) calculations by Smith and Mattheiss,[12] and then inserting relativistic corrections. Where necessary, the widths of the d bands were adjusted until the peak positions of the EDJDOS reasonably matched those in the UPS data.

The DOS on each of these metals was generated as a by-product of the k-space integrations involved in the calculation of the EDJDOS. These integrations were performed by a Monte Carlo sampling of 250,000 points in the irreducible $\frac{1}{48}$th wedge of the BZ. The results for the DOS are shown in Figs. 1 and 2 for the $4d$ and $5d$ metals, respectively. The parameters of the combined interpolation scheme used to generate the energy eigenvalues are to be found in Table II of III. These densities of states will be compared with high-resolution XPS data in Sec. III B. It should be emphasized that no XPS data whatsoever have been used in the parameterization of the model band structures. Empirical adjustments were made only to improve the fit with UPS data.

Figures 1 and 2 show the unoccupied densities of states up to 12 eV above the Fermi level, i.e., the accessible range of conventional UPS experiments. The structure in this energy range is quite pronounced, particularly in the case of Rh and Pd. The edges at 8.3, 7.3, 3.5, 7.1, 5.9, and 3.2 eV in Rh, Pd, Ag, Ir, Pt, and Au, respectively, correspond to the onset of contributions to the DOS from band 7. As discussed in III, strong contributions occur also in the EDJDOS at photon energies where band 7 becomes available as a source of final states. Some of these have been observed experimentally in the UPS studies reported in II. In XPS, however, the final energy is so large that the final density of states is expected to be relatively featureless and to have no influence on the form of the spectrum.

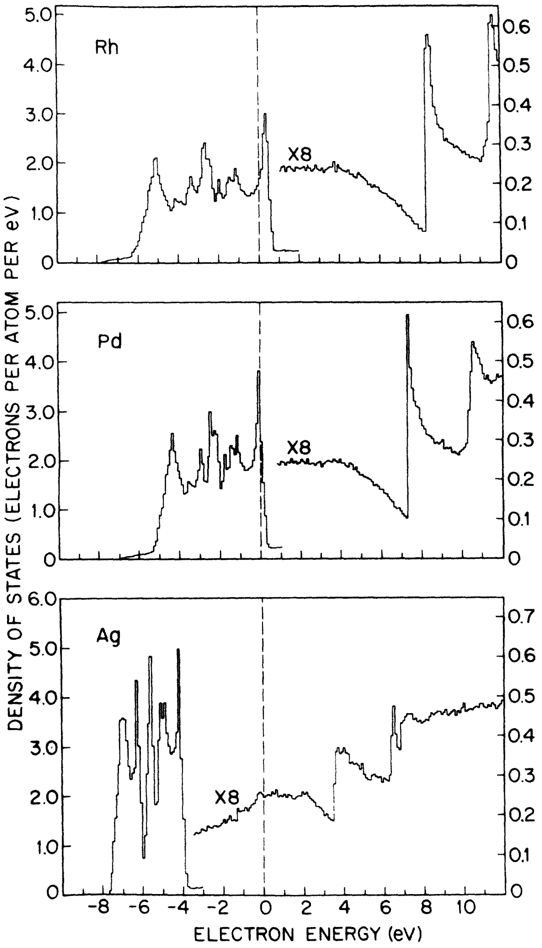

FIG. 1. Density-of-states histograms for the $4d$ metals, Rh, Pd, and Ag, calculated from the model band structures described in Ref. 2. The zero of energy corresponds to the Fermi level.

III. XPS RESULTS AND COMPARISONS WITH BAND THEORY

A. Experimental details

The x-ray photoelectron spectra were obtained on a Hewlett-Packard 5950A ESCA (electron spectroscopy for chemical analysis) spectrometer using monochromatized Al $K\alpha$ radiation. The instrumental resolution, estimated from the cutoff at the Fermi edge of silver, is 0.5-eV full width at half-maximum (FWHM). The form of the instrumental slit function was not known accurately at the time of this work. Least-squares fittings of narrow lines like the $4f$ doublet of Au requires a function whose shape is intermediate between Gaussian and Lorentzian, presumably representing both instrumental and lifetime contributions. The width of the $4f$ lines was 0.73-eV FWHM. A small asymmetry, characterized by a tailing-out to greater binding energy, was also detected, but is known to arise in Au from the presence of inelastically scattered photoelectrons.

Two methods of sample preparation were employed. The first, used for Ir and Ag, consisted of sputter-ion cleaning of high-purity polycrystalline foils. These samples were cleaned initially with solvents and then by argon-ion sputtering in the sample preparation chamber of the spectrometer. The cleaning process was monitored by checking the oxygen and carbon $1s$ lines associated with the absorbed surface layer. The residual carbon and oxygen signals correspond to only a small fraction of a monolayer of contamination.

The sputtering procedure was found to work quite well except in the case of Pd. For this metal, and also Rh, Pt, and Au, samples were prepared by evaporation from tungsten boats in a vacuum of 10^{-8} Torr. The XPS data obtained in some of

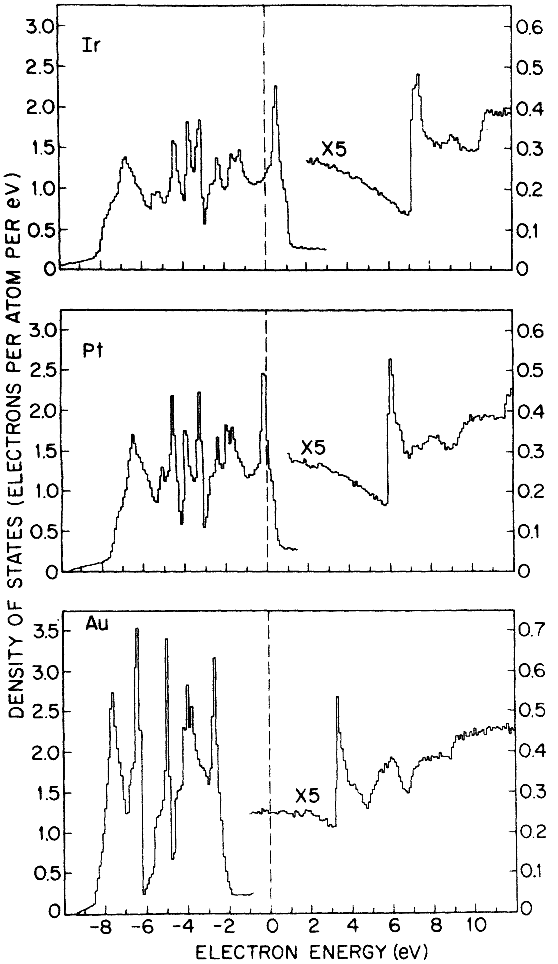

FIG. 2. Density-of-states histograms for the $5d$ metals, Ir, Pt, and Au, calculated from the model band structures described in Ref. 2. The zero of energy corresponds to the Fermi level.

these metals have been reported previously by Hüfner *et al.*,[9,13] and those for Au and Rh were taken from Ref. 9. In those papers it is shown that XPS spectra on evaporated films of Pd display a well-defined Fermi edge and appreciable structure in the d-band region. If the same samples are exposed to argon-ion sputtering, however, the XPS spectra lose their well-defined Fermi edges and become featureless, similar to the situation reported for Pd by Pollak *et al.*[14] It has been hypothesized by Hüfner *et al.*[13] that damage induced by bombardment with argon ions creates a low-density, perhaps amorphous, surface layer on Pd. Interestingly, the spectrum obtained on evaporated Pd is closer in shape to those obtained earlier by Hüfner *et al.*[15] using less painstaking cleaning methods. In all the experimental spectra considered here, the Fermi edges in the spectra are well defined, so we may safely assume that the damage effect is not severe. However, we cannot rule out completely the possibility that some structure has been lost, particularly in Rh, Ir, and Pt which have the higher melting points. It would be desirable, in some future study, to perform XPS measurements on samples of these metals evaporated by electron bombardment, as was done in UPS studies of these metals.[1]

To facilitate comparison between the XPS curves and the calculated densities of states, the data were corrected for the background due to inelastically scattered electrons. The approximation adopted is that the background at a given energy is proportional to the integral of the spectrum from that energy to the Fermi energy. This correction was applied to the data by an iterative computer routine. The corrections are relatively small, and do not significantly influence the positions of peaks in the spectra. They are, however, of some significance when we wish to compare the intensities in the spectra with calculated densities of states.

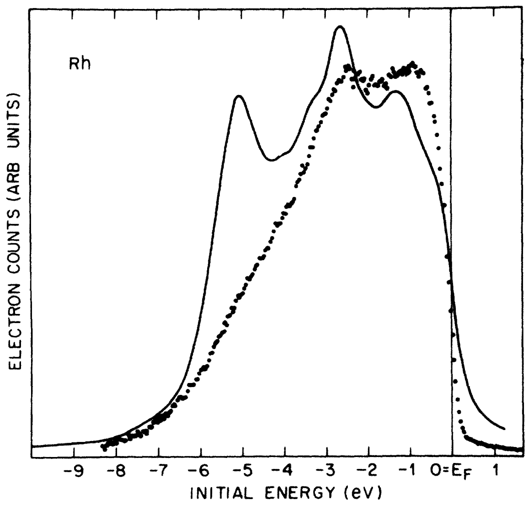

FIG. 3. XPS data on Rh (closed circles) compared with a smoothed version of the occupied DOS.

B. Comparison with densities of states

Taking each of the metals in turn, in Figs. 3—8 we compare the measured XPS spectrum with the calculated occupied density of states. The DOS curves have been smoothed with a Lorentzian broadening function of 0.5-eV FWHM. The normalization of the XPS data with respect to the DOS curves is arbitrary, but has been chosen so as to obtain an approximate match in the region a few eV below the Fermi level. It will be seen that this choice leads to a discrepancy between the relative intensities in the region further below the Fermi energy. This discrepancy occurs consistently throughout the series of metals considered here.

Rhodium

The XPS valence spectrum for Rh is shown in Fig. 3. The peak at −2.5 eV and the valley centered at about −1.8 eV in the experimental data coincide quite well with the peak and valley at − 2.7 and − 1.8 eV, respectively, in the smoothed DOS also shown in Fig. 3. The broad peak centered at −1.0 eV in the XPS data correlates reasonably well with the DOS peak at −1.3 eV but does not seem to resolve it from the −0.3-eV shoulder in the DOS. The very prominent peak at −5.1 eV in the DOS does not appear strongly in the XPS. There is, however, a discernible bulge in the XPS data in the energy region around −5.1 eV. The break in slope of the XPS data at about −3.8 eV correlates reasonably well with the valley in the DOS at −4.3 eV.

Palladium

The DOS curves and the XPS data on Pd are shown in Fig. 4. The peaks at −1.3 and −2.4 eV in the calculated DOS coincide closely with features at the same energies (indicated by the broken vertical lines) in the XPS data. The prominent shoulder at −0.3 eV in the DOS curve corresponds to the peak at −0.6 eV in the XPS data. This high-energy feature is more prominent in Pd than in Rh because of band-filling effects. Referring back to Fig. 1, we see that in Pd the addition of an extra electron means that the occupied states include part of the very sharp peak at the top of the d-band DOS. The strong peak at − 4.3 eV in the DOS coincides with a bulge in the XPS data, indicated by a broken vertical line. As in Rh, the relative intensity of this low-energy feature is much smaller in the XPS data than in the DOS.

The coincidence between the theoretical and

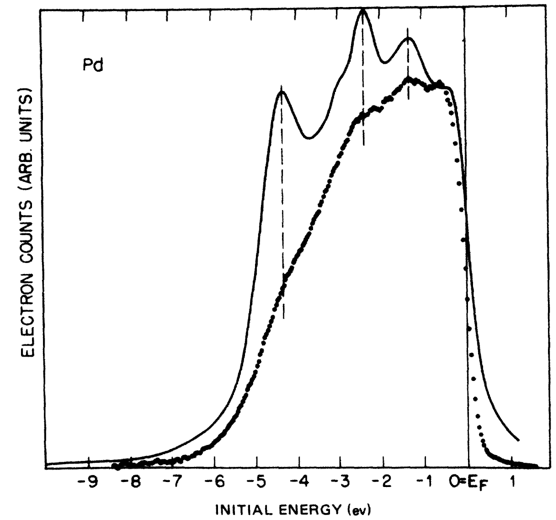

FIG. 4. XPS data on Pd (closed circles) compared with a smoothed version of the occupied DOS.

experimental structures in Fig. 4 is quite satisfactory. It is to be noted that this correspondence occurs only with the data obtained on evaporated films, and does not occur with data obtained on samples cleaned by sputtering.[13,14]

Silver

The experimental and theoretical results on Ag are shown in Fig. 5, and the agreement between them is perhaps the best of the metals under discussion here. Peaks at − 4.9 and − 6.3 eV in the DOS coincide with peaks at the same energy in the XPS data. The shoulder at − 4.3 eV in the DOS has its counterpart in the XPS data. The deep valley at −6.0 eV in the DOS corresponds closely to the valley at −5.9 eV in the XPS data; as mentioned elsewhere,[6] this valley appears strongly in the DOS only when spin-orbit effects are included. Peaks in the DOS at −5.5 and −6.8 eV correspond to weaker features in the XPS data at the same energies as indicated by the broken vertical lines. The weakness in the experimental data of the structure at −5.6-eV may also account for the slight discrepancy in the energy location of the valley mentioned above. If the −5.6-eV peak in the unsmoothed DOS were artificially weakened, the effect, after smoothing, would be to shift the valley at −6.0 eV in the DOS closer to the value of −5.9 eV observed experimentally. Note once again that the low energy structure at −6.9 eV is more intense in the DOS than in the XPS data. The relative intensity of the DOS is also greater in the *s-p* region, which extends from about −4 eV to the Fermi energy.

The DOS shown in Fig. 5 differs somewhat from that presented in an earlier study of Ag.[16] In that work, a model band structure was constructed by fitting the first-principles APW calculations of Snow.[17] The position and width of the *d* bands were then adjusted so as to optimize the fit between the DOS and the XPS data. In the fitting procedure of that paper we were strongly influenced by a desire to fit the upper edge of the *d* bands at about − 4 eV and, also, the lower edge of the *d* bands between −7 and −8 eV. It will be appreciated from an inspection of Fig. 5 that this procedure would lead to a *d*-band width which is smaller than that used here. Indeed, the *d* bands in our present model band structure are about 5% wider than in the earlier study. It should be reemphasized that the model band structure used here was not fitted to the XPS data in any way, but was adjusted only to agree with UPS data as reported in III.

Iridium

Having discussed the 4*d* metals, we now turn to the 5*d* metals, and our results for Ir are shown in Fig. 6. The smoothed DOS may be divided for convenience into three energy regions separated by the prominent valleys at − 2.9 and − 5.7 eV. The latter, indicated by the broken vertical line, coincides in energy with a break in slope of the XPS data. We identify the DOS valley at −2.9 eV with the valley at − 3.2 eV in the XPS data. In the upper energy region, the DOS peak at −1.5 eV coincides with an XPS peak at the same energy, and the DOS shoulder at −0.3 eV has its counterpart in the XPS data at about −0.5 eV; the DOS peak at −2.4 eV may correspond to the weak XPS structure at about −2.8 eV. In the middle energy region between −2.9 and −5.7 eV, the DOS curve shows two well-defined peaks and some other detailed substructure;

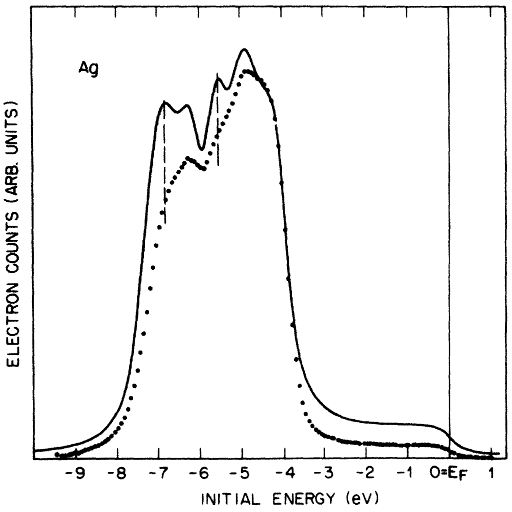

FIG. 5. XPS data on Ag (closed circles) compared with a smoothed version of the occupied DOS.

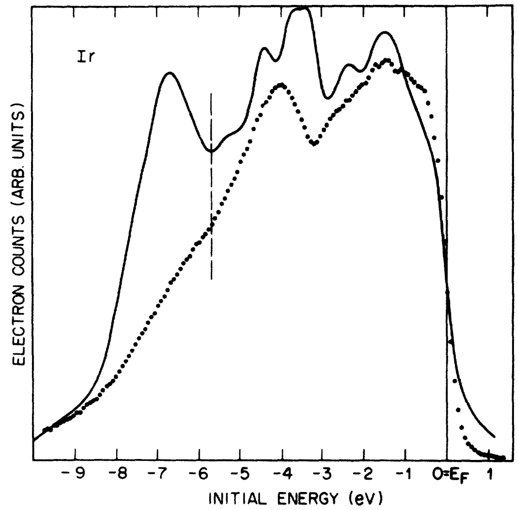

FIG. 6. XPS data on Ir (closed circles) compared with a smoothed version of the occupied DOS.

we will argue in Sec. IIIC that in the case of Pt the details in this region are sensitive to the inadequacies of the combined interpolation scheme; it is proposed that the two main peaks should be lumped together as a composite peak which we then identify with the strong peak in the XPS data at −4.0 eV. In the low-energy region, we see that the strong DOS peak centered at −6.7 eV corresponds to a much less intense bulge in the XPS data spanning the same energy range.

Platinum

Our results on Pt are shown in Fig. 7. The comparison between the DOS curve and the XPS data appears, at first sight, much less encouraging than in the metals discussed above. It will be shown below, however, that some of the details of the DOS curve are particularly sensitive to the crudities of the combined interpolation scheme. The comparison is seen in a more favorable light if we group some of the structures as we did above in the case of Ir. We divide the smoothed DOS curve into three energy regions separated by the prominent valleys at −2.9 and −5.4 eV. The latter, indicated by a broken vertical line, coincides in energy with a discernible concavity in the XPS data. We identify the DOS valley at −2.9 eV with the valley at −3.3 eV in the XPS data. In the middle energy region between −2.9 and −5.4 eV, the DOS curve shows three peaks and a pronounced valley at −4.2 eV which, disappointingly, coincides almost exactly with a peak in the XPS data; following our procedure in Ir, however, we lump all the peaks into a composite peak which we identify with the broad peak in the experimental spectrum centered at about −4.2 eV; the justification for this procedure will be presented in Sec. IIIC. Having disposed of this middle energy region, the upper and lower energy regions display reasonable agreement between theory and experiment. In the upper energy region, the strong DOS peak at −1.8 eV coincides with an XPS peak at the same energy; the DOS peak at −0.3 eV coincides with a shoulder in the XPS data at the same energy. In the low-energy region, the strong DOS peak centered at −6.3 eV corresponds to a just-discernible feature in the XPS data spanning the same energy range.

Gold

The experimental and theoretical results on Au are shown in Fig. 8, and the comparison is not as good as in the other metals. The DOS peaks at −2.8 and −3.9 eV coincide closely with experimental peaks at −2.8 and − 3.8 eV. At lower energies, however, the closeness of the correspondence deteriorates. A particular discrepancy on which we will concentrate concerns the very prominent peak at −6.2 eV in the experimental spectrum. We identify this peak with the DOS peak at −6.5 eV.

C. Spin-orbit adjustments

The results of the comparisons in Sec. IIIB may be summarized as follows. In the 4*d* metals, Rh, Pd, and Ag, the positions of structure in the DOS coincide remarkably well with structures in the high-resolution XPS data. In the 5*d* metals, the correspondence tends to deteriorate, the worst discrepancies occurring in Pt and Au.

One of the motivations for the present work was the hope that many-body effects or surface selectivity effects might manifest themselves as such discrepancies. Some caution should be exercised here, however. Indeed, we will argue

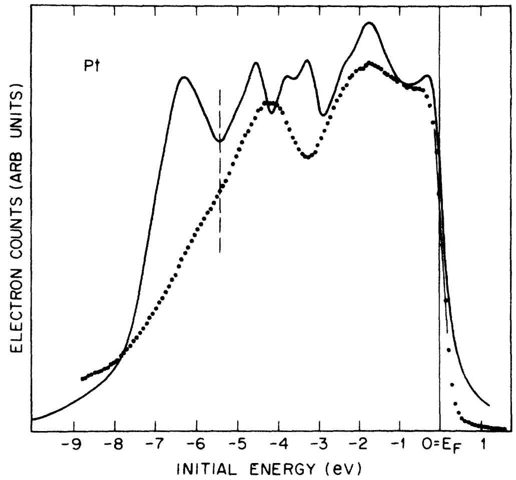

FIG. 7. XPS data on Pt (closed circles) compared with a smoothed version of the occupied DOS.

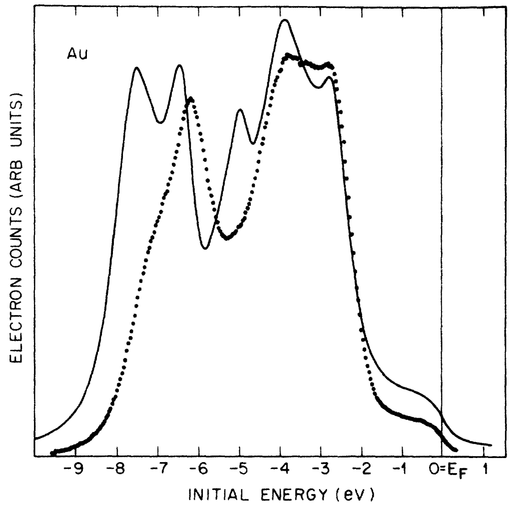

FIG. 8. XPS data on Au (closed circles) compared with a smoothed version of the occupied DOS.

that the worst of the discrepancies in Pt and Au are more likely due to the inadequacies of our combined interpolation scheme. We shall focus, in particular, on the approximate method of inserting spin-orbit splitting into the scheme.

In an earlier paper,[12] it was found that the rms-fitting error of the combined interpolation scheme increased monotonically with the width of *d* bands. This helps to explain why the discrepancies noted above occur in the 5*d* metals, while the 4*d* metals show good agreement. In addition to the width of the *d* bands, another important factor is the spin-orbit parameter, which is also bigger in the 5*d* metals, Ir, Pt, and Au, than it is in the 4*d* metals, Rh, Pd, and Ag.

So far, we have been using without modification the model band structures presented in III. The only empirical adjustments contained in these band structures were made to the width of the *d* bands in order to improve the fit to UPS data. No adjustments were made to fit XPS data, and the spin-orbit parameter was set equal to the atomic value given by Herman and Skillman.[18] We now depart from this procedure and, in the cases of Pt and Au, investigate whether varying the spin-orbit parameter improves the agreement with XPS data.

Platinum

The effects of reducing the spin-orbit parameter in Pt from its atomic value of 0.046 to 0.038 Ry is shown in Fig. 9. The agreement between the smoothed DOS and the experimental XPS data is improved appreciably, and the comparison is now very similar to the one for Ir shown in Fig. 6. The valley in the DOS of Fig. 9 at −4.0 eV is less pronounced than the corresponding valley in Fig. 7. We are therefore more justified in lumping the structures between the DOS valleys at −2.8 and −5.4 eV into a composite structure, and then identifying it with the peak at −4.2 eV in the XPS data.

The detailed structure of the DOS in the middle of the *d*-band energy range appears to be particularly sensitive to the details of the energy bands. This is rather surprising since the DOS represents an integral over the entire BZ, and one might suppose that fine details would be averaged away. To obtain an estimate of this sensitivity, it is instructive to compare the unsmoothed DOS for Pt shown in Fig. 2 with that calculated by Mueller *et al.*[19] using a very similar combined interpolation scheme.

The unsmoothed DOS of Pt shown in Fig. 2 displays two deep minima of comparable strength at −3.0 and −4.1 eV. The unsmoothed DOS of Mueller *et al.* has a deep minimum at −3.3 eV, which seems to correspond to the −3.0-eV minimum of the present calculation, but has no strong feature corresponding to our −4.1-eV valley. Such deep minima arise after the insertion of spin-orbit splitting. However, the strength, and even the existence, of such minima would seem to depend on a subtle interplay between spin-orbit effects and the effects of hybridization; we note in this regard that one of the main differences between the present parameterization of the combined interpolation

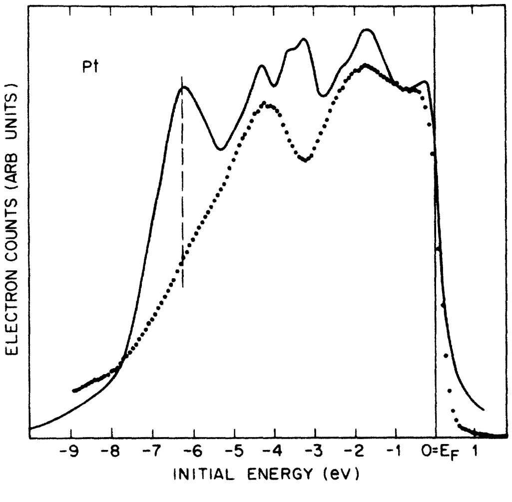

FIG. 9. XPS results on Pt (closed circles) compared with the results of a modified DOS calculation (smooth curve). The model band structure used here differs from that in Fig. 7 in that the 5*d* spin-orbit parameter has been reduced from 0.046 to 0.038 Ry; the parameter E_0, representing the center of gravity of the *d* bands, has been raised by 0.004 Ry; all other parameters remain the same.

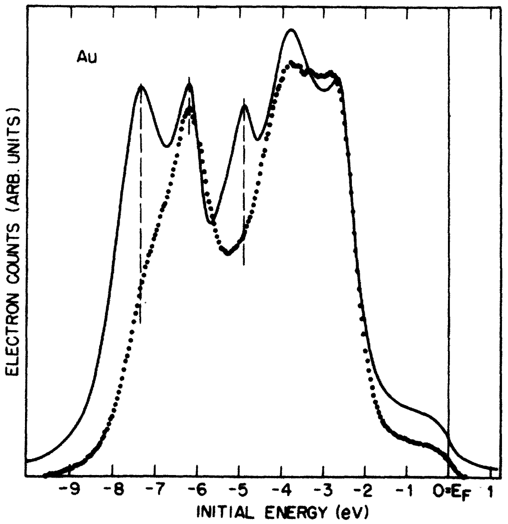

FIG. 10. XPS results of Au (closed circles) are compared with the results of a modified DOS calculation (smooth curve). The model band structure used here differs from that in Fig. 8 in that the $5d$ spin-orbit parameter has been reduced from 0.053 to 0.045 Ry; the parameter E_0, representing the center of gravity of the d bands, has been raised by 0.004 Ry; all other parameters remain the same.

scheme and that of Mueller[20] concerns the way in which the hybridization between the d-states and plane-wave states is cut off at large k. A smoothed version of the DOS of Mueller *et al.* would reproduce quite well the minimum in the experimental XPS data at −3.3 eV (see Fadley and Shirley in Ref. 5). As far as the present investigation is concerned, we conclude that the −4.1-eV valley in the Pt DOS is likely to be a spurious feature due to inadequacies of the interpolation scheme and should be ignored. Likewise, in Ir, we propose that the similar minimum at about −4.0 eV in the DOS results of Figs. 2 and 6 should also be ignored. We offer this as justification for the procedure adopted above, where we lumped the structures in this middle d-band region into a single composite peak.

Gold

In Fig. 10 we show the results for the DOS obtained by reducing the spin-orbit parameter from its atomic value of 0.053 to 0.045 Ry. In this calculation on Au, as well as in the calculation above on Pt, the adjustments to the spin-orbit parameter were accompanied by adjustments to E_0, the center of gravity of the d bands, so as to maintain the upper edge of the d bands at a constant position. It is seen in Fig. 10 that the correspondence between structures in the DOS data and those in the XPS data represents an appreciable improvement over that shown in Fig. 8. In particular, we have arranged for the XPS peak at −6.2 eV to coincide precisely with a DOS peak at the same energy. The DOS peaks at −2.7 and −3.8 eV coincide, respectively, with peaks at −2.8 and −3.8 eV in the XPS data. The strong DOS peak at −7.3 eV corresponds to a discernible bulge in the XPS data at about the same energy. The DOS peak at −4.9 eV, however, has no counterpart in the XPS data. A very similar situation occurs in the Ag results of Fig. 5, where a strong DOS peak at −5.6 eV is seen only weakly in the XPS. It may be that this is another DOS feature whose strength is exaggerated by imperfections in the details of the interpolation scheme.

IV. SUMMARY AND CONCLUSIONS

The aim of the present work has been to perform a detailed comparison of XPS, UPS, and band theory for the d-band metals, Rh, Pd, Ag, Ir, Pt, and Au. The procedure has been to take model band structures, which have been shown in III to give reasonable agreement with UPS, and to investigate whether they give equally good agreement with XPS.

In the $4d$ metals, Rh, Pd, and Ag, the energy positions of structure in the XPS data are found to agree remarkably well with those in the calculated DOS. The agreement is particularly gratifying in the cases of Rh and Pd, where no empirical adjustments had been made to the width of d bands. The only corrections made to the first-principles calculations of Mattheiss[12] on these two metals were for relativistic effects.[2] In the $5d$ metals, Ir, Pt, and Au, the agreement between positions of structures in the XPS data and those in the smoothed DOS is poorer than that in the $4d$ metals, particularly in the middle d-band region. We have argued, however, that the worst discrepancies are most likely due to imperfections in the interpolation scheme, such as the approximations involved in the simulation of spin-orbit splitting and hybridization effects.

We find in Pt and Au that improved over-all agreement between UPS, XPS, and band theory is obtained by the use of a spin-orbit parameter which is 0.008 Ry less than its atomic value. No particular physical significance should be attached to this, however, since it has been shown by Andersen[21] that the spin-orbit parameter actually increases with increasing energy across the d bands. Workers concerned more with the behavior of the energy bands at the top of the d bands, as in Fermi-surface studies, are likely to find that a value of the spin-orbit parameter greater than the atomic value is more appropriate. As far as XPS is concerned, it is of interest to note that the shape of the DOS in the upper d-band region is relatively insensitive to changes of the spin-orbit parameter. The improvements in the middle d-band region have therefore been obtained without sacrificing the agreement already obtained in the upper d-band region. We find a similar situation in connection with the comparisons between the EDJDOS and UPS results which, because of the more restricted energy range of UPS, tend to concentrate attention on the upper d bands. Optimizing the fit of UPS to the upper d bands could sacrifice the fit of XPS to the lower d bands, and vice versa. The EDJDOS obtained for Pt and Au using the adjusted spin-orbit parameter, however, is found to be in equally reasonable agreement with the UPS data of II as the EDJDOS obtained using the atomic spin-orbit parameter. A principal conclusion of our study, therefore, is that, within the limitations imposed by (i) the imperfections of the interpolated band structures and (ii) experimental resolution, we find no significant difference between the occupied energy bands "seen" in XPS and UPS experiments.

In the case of Au, a comparison between UPS, XPS, and band theory of the kind attempted here can be made by inspection of previous papers by Shirley[22] and by Christensen.[23] Shirley has shown that the XPS curve for Au bears a strong resemblance to the DOS obtained from a first-principles relativistic APW band-structure calculation by Christensen and Seraphin.[24] Christensen[23] has further shown that the EDJDOS obtained from the same band structure agrees well with UPS data. There are, however, some slight discrepancies in the energy region below -4 eV; the structures in the higher-derivative UPS curves occur at somewhat lower energies than the corresponding structures in the EDJDOS. We note from Fig. 12 of Ref. 23 that, without sacrificing the agreement above -4 eV, these discrepancies could be largely removed by a slight stretching of the d bands. Interestingly, such an adjustment would also improve the comparison between the DOS and the XPS data in Fig. 5 of Ref. 22. These observations confirm our conclusion that there exists a band structure capable of explaining the energy locations of structures in both the UPS and the XPS data. Likewise in Cu, previous work has shown that the band structure calculated from the Chodorow potential gives both a DOS in close agreement with XPS results[16] and an EDJDOS in good agreement with UPS results.[25,26]

Turning now to intensities rather than positions of structures, a significant discrepancy is found between XPS data and DOS curves. The relative intensity of the XPS data towards the bottom of the d-band region is consistently lower for all the metals considered here than is predicted by the DOS alone. Compared with other DOS calculations,[16] the present scheme may tend to exaggerate the strength of the lowest energy peak in the d-band DOS, but this effect is not large enough to explain the discrepancy. The intensity differences can be explained if we postulate an optical-transition strength which varies across the d bands, being small at the bottom of the d bands and large at the top. In support of this suggestion, we note that it is the lower d bands which hybridize most strongly with the s-p bands.[27] In Ag and Au (Figs. 5, 8, and 10) relative intensity of emission from the s-p-like states between the top of the d bands and the Fermi level is also lower in the XPS data than it is in the DOS. Finally, we note that because of the relative attenuation of the low-energy end, the FWHM of the XPS valence-band spectrum (sometimes quoted as a measure of the d-band width) is actually an underestimate of the true width of the occupied. d bands.

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