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Photoemission Studies of Platinum†

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Photoelectron energy-distribution curves of Pt at photon energies $6.8 \leq \hbar\omega \leq 11.6$ eV exhibit structure originating from initial states 3.6, 2.5, 1.5, and between 0.7 and 0.2 eV below E_F. A strong peak at -0.2 eV observed for $\hbar\omega < 9.1$ eV is joined by a second peak at -0.7 eV in the range $\hbar\omega = 9.1$–9.7 eV. Above 9.7 eV, the two peaks merge to a single rounded peak at -0.5 eV which grows stronger and sharper at higher photon energy. Good correspondence is found between structure in the energy-distribution curves and in a calculated band density of states. The results are discussed in terms of the direct and nondirect models of optical excitation and compared to similar results from Ni, Pd, and Rh.

I. INTRODUCTION

It is now well established that photoemission studies can give valuable information on the electronic structure of solids. In this paper we present data obtained from carefully prepared Pt samples. Earlier studies of Pt by Yu and Spicer[1] were hindered by poor vacuum conditions. In discussing the experimental results we compare the photoelectron energy-distribution curves (EDC) obtained in this work with the theoretically calculated valence-band density of states of Mueller *et al.*[2] Finally, as a link to the systematic study of transition metals, we compare the present work to results from Rh,[3] Pd,[4] and Ni.[5]

II. EXPERIMENTAL PROCEDURE

Photoelectron EDC's were obtained from Pt films electron-gun evaporated onto quartz substrates. The data presented in this paper are from a film approximately 600 Å thick. During the evaporation, the pressure changed from a base pressure of 10^{-10} to 1.5×10^{-8} Torr. A subsequent x-ray diffraction analysis displayed only peaks appropriate to an fcc crystal of (111) orientation.

The energy spectra of photoemitted electrons were measured with a three-electrode high-reolution energy analyzer.[6] In this analyzer, a screen forms a field-free drift region around the emitter. The electrons are then retarded at the nearly spherical equipotential surfaces between the screen and the collector. The resolution error of the analyzer is estimated to be 2.8% of the electron kinetic energy.[7] The EDC's were obtained by differentiating the current-retarding voltage curve by a previously described ac technique.[8,9]

III. RESULTS

In Fig. 1 we compare the EDC's from this work to the EDC's obtained in the earlier work of Yu and Spicer. As can be seen, the position of structure is about the same in the two sets of curves.[10] However, the high-energy or "leading" photoelectron peak is much stronger in our results than in the earlier work in which EDC's were obtained from films evaporated at 8×10^{-8} Torr. It is well established that the electron-electron scattering length becomes smaller as the electron energy increases. Thus, as the photon energy is increased, the electrons in the leading peak come from closer and closer to the metal surface. The fact that the leading peak in the curves of Yu and Spicer degrades with increasing photon energy may indicate that the band structure near the metal surface has been

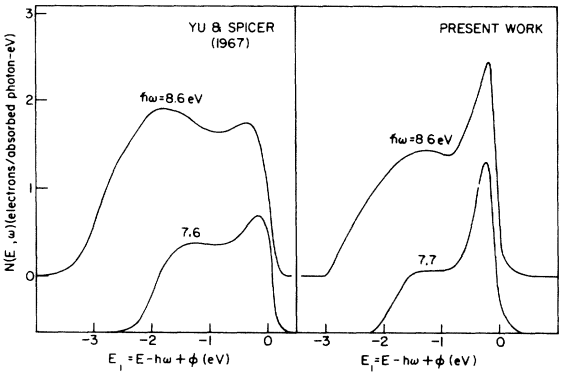

FIG. 1. Comparison of EDC's from the present work and the previous work of Yu and Spicer. Note the relatively fewer number of low-energy electrons in EDC's obtained from the better samples of the present work (normalized to the yield).

modified by chemical or alloying action between the Pt and impurities on the surface. The foreign atoms on the surface may diffuse a few angstroms into the Pt. The irregular nature of these effects cause a smearing of the Pt electronic structure. Another effect which may be important is an increase of the electron scattering such that more electrons are simply scattered out of the high-energy peak.

The EDC's in this work have been normalized to the measured quantum yield which is shown in Fig. 2. The reflectance measurements of Yu, Spicer, and Hass[11] were used in calculating the yield per absorbed photon.

In Fig. 3 we show our EDC's from the Pt film for photon energies ranging from 6.8 to 11.6 eV. The curves are plotted with respect to the initial-state energy of electrons, $E_i = E - \hbar\omega + \Phi$, where E is the kinetic energy of the emitted electrons and Φ is the work function. The Fermi energy corresponds to $E_i = 0$. The work function was 5.6 ± 0.15 eV, as determined from considerations of the width of the EDC's corrected for instrumental broadening. For photon energies below 7.7 eV, the EDC's exhibit only one sharp peak at about 0.2 eV below the Fermi level E_F. At 7.7 eV, a shoulder appears

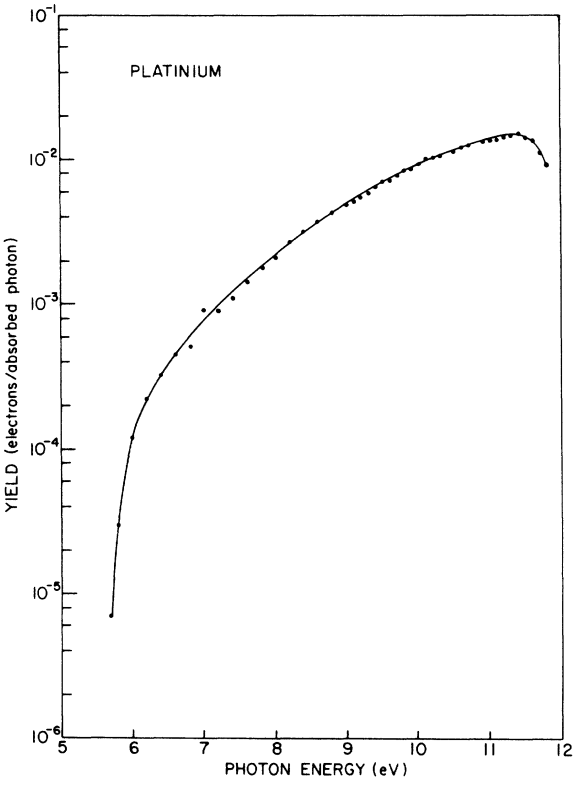

FIG. 2. Absolute spectral distribution of quantum yield of Pt.

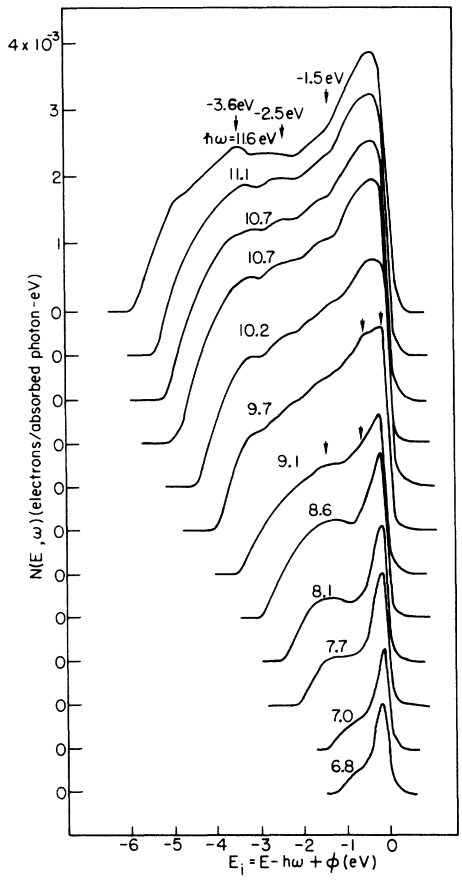

FIG. 3. EDC's from an electron-gun evaporated thin film over a photon energy range $6.8\ \text{eV} \leq \hbar\omega \leq 11.6$ eV. The EDC's are plotted with respect to initial-state energy $E_i = E - \hbar\omega + \varphi$.

1.5 eV below E_F. At $\hbar\omega = 9.1$ eV, a shoulder at -0.7 eV appears and grows stronger until at $\hbar\omega = 9.7$ eV there are two closely spaced peaks of approximately equal strength. For photon energies greater than 9.7 eV, the two peaks nearest the Fermi energy appear to merge into a single peak 0.5 eV below E_F. This peak is somewhat flattened at 10.2 and 10.7 eV and then increases in sharpness and strength at still higher photon energies. There are three other pieces of structure apparent in the EDC's above $\hbar\omega = 9.7$ eV. A shoulder at -1.5 eV is still quite apparent at $\hbar\omega = 10.2$ and 10.7 eV but becomes weaker and at 11.6 eV is obscured by the trailing edge of the now very strong peak near the Fermi level. There is a striking increase in the strength of the high-energy peak relative to the low-energy structure as the photon energy increases. Structure can also be distinguished at -2.5 eV. In addition, at $\hbar\omega = 11.1$ and 11.6 eV the photon energy is high enough so that a peak at -3.6 eV previously obscured by the escape function is now apparent.

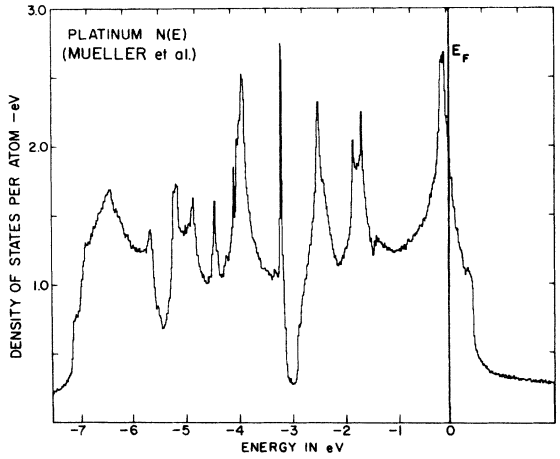

FIG. 4. Band density of states for Pt calculated by Mueller *et al.* (Ref. 2).

At $\hbar\omega = 11.6$ eV there is also a hint of structure at -5 eV.

IV. DISCUSSION

The structure at -1.5, -2.5, and -3.6 eV in the EDC's of Fig. 3 (even though not extremely well defined) remains relatively constant in initial-state energy over a wide range of photon energy. Such behavior can be explained well by the nondirect model in which $\vec{k}$ is not conserved in the one-electron sense. Moreover, theoretical calculations including many-body effects[12] indicate that nondirect transitions can be expected to be important in a *d*-band metal such as Pt. In some metals, structure constant in initial-state energy has been accounted for by the direct-transition model[13] and in the absence of calculated EDC's the direct-transition model cannot be ruled out. The strong structure within 1 eV of the Fermi level in Fig. 2 varies in strength and position with photon energy and is quite likely due to direct transitions.

In the case of both direct transitions (especially in metals[14,15]) and nondirect transitions,[16] a correspondence between the EDC's and the density of states from an energy-band calculation has frequently been observed. The strong peaks in the calculated Pt density of states shown in Fig. 4, are tabulated and compared to structure in the EDC's in Table I. Peaks in the density of states at -3.2 and -4.4 eV are not included in Table I because their integrated strength is small compared to the included peaks. Although the positions of the EDC peaks compare rather well, only the leading peak in the EDC (0.2–0.7 eV) is comparable in strength to the density-of-states peak. The peaks in the EDC's well below the Fermi level are much weaker than the corresponding peaks in the calculated density of states. This may be a result of the many-body effects which produce the nondirect transtions.

TABLE I. Position of structure.

EDC	Band density of states
$-0.2 - 0.7$	-0.14
-1.5	-1.7
-2.5	-2.5
-3.6	-4.0
-5.0	-5.0

One of the most interesting features of the EDC's from Pt is the behavior of the strong leading peak due to electrons excited from initial states in *d* bands near the Fermi level. As indicated above, there is a strong peak in the calculated density of states 0.14 eV below E_F which corresponds quite well with the peak in the EDC's 0.2 eV below E_F at photon energies less than 9.1 eV. At higher photon energies, a second peak at -0.7 eV merges with the peak at -0.2 eV to a single peak which sharpens with increasing photon energy. Similar behavior, which we attribute to direct transitions, has been observed in Rh[3] and Pd,[4] as seen in Fig. 5. The transition from a rounded to a sharp leading peak is particularly apparent in the Rh EDC's. It

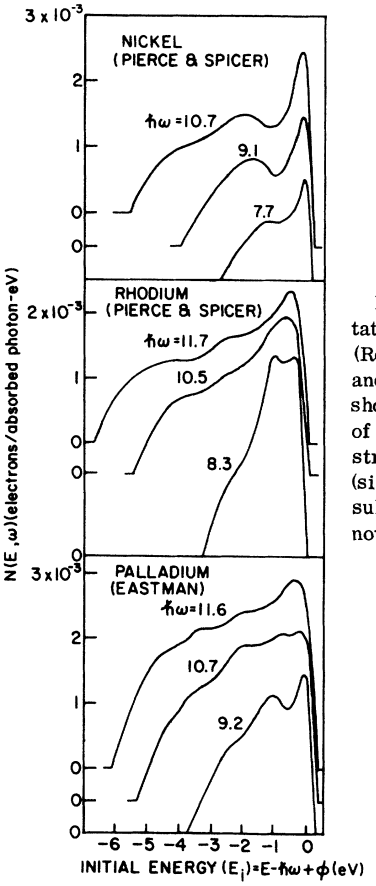

FIG. 5. Representative EDC's from Ni (Ref. 5), Rh (Ref. 3), and Pd (Ref. 4) which show the development of the double-peaked structure near E_F (similar to the Pt results) in Pd and Rh but not Ni.

is interesting to note that Ni[5] (see Fig. 5), which is isoelectronic to Pt and Pd, exhibits a single strong leading peak which remains 0.2 eV below E_F and does not exhibit the double-peaked behavior so suggestive of direct transitions.

V. CONCLUSIONS

High-resolution photoelectron EDC's have been obtained from an electron-gun evaporated thin film of pure Pt. Comparison of experimental EDC's and a calculated band density of states shows that the position of each major structure in the calculated density of states is within a few tenths of an eV of a piece of structure in the EDC's. Calculated EDC's using the interpolated bands of Mueller *et al.*[2] and assuming direct transitions would be very useful in determining whether the slight mismatch of structure in the calculated density of states and structure in the EDC's is suggestive of changes required in the calculations or whether it is merely indicative of the influence of matrix elements, including k conservation, on the optical excitations. Such calculated EDC's would further our understanding of electronic transitions in Pt and indeed would test our direct-transition interpretation of the behavior of the leading peak in the EDC's. The similarities pointed out between Pt, Pd, and Rh suggest that progress in understanding one of the metals will assist in understanding the others. It is interesting to note (see Fig. 5 and Sec. IV) that Ni behaves differently from Pt, Pd, and Rh in this regard. The highest photon energy used in our experiments, 11.6 eV, was limited by the cutoff of the LiF window. We expect that experiments over a continuous range of higher photon energies will be very valuable and may soon be possible with the increasing development of synchrotron radiation as a high-vacuum source of ultraviolet and soft-x-ray radiation.[17]

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