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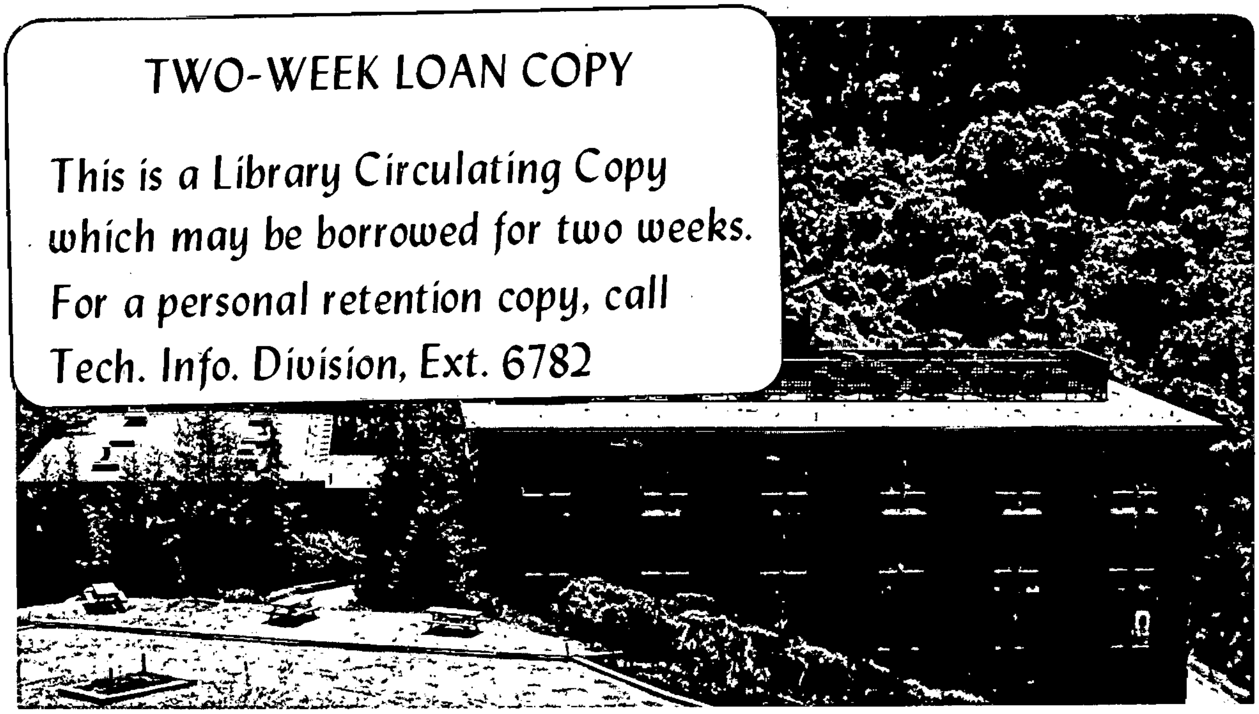

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AN ANGLE-RESOLVED PHOTOEMISSION DETERMINATION OF THE BAND-STRUCTURE OF PLATINUM BETWEEN Γ AND X

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ABSTRACT

Synchrotron radiation was used to record angle-resolved normal photoemission spectra of Pt(100) in the photon energy range 6 eV $\leqslant h\nu \leqslant$ 32 eV. Features were observed in the spectra that arise from both direct transitions and the one-dimensional density of states. Intensity resonances associated with final-state structure near Γ were observed, in accord with earlier data reported for Pt(111). The direct-transition features were used to derive an empirical valence-band structure of Pt between Γ and X, which is in generally good agreement with an existing RAPW calculation.

Introduction

The study by angle-resolved photoemission (ARP), in conjunction with the use of synchrotron radiation, of crystal faces of the Group II-B and III-B metals has been the subject of a number of investigations.[1-4] It is now fairly well-established that the direct transition model, along with a judicious choice of final state, can be used to determine dispersion relations from such data. However, the particular choice of final state is somewhat *ad hoc* in nature. Attention is now being focused on this problem, especially for photon energies where photoemission corresponds to a gap in the bulk conduction bands.[3-5] Recent ARP studies of various low Miller-index faces of Ag,[3] Au,[4] and Pt[4] suggests that a quasi-free-electron final state can be used even when such a gap exists.

The present work represents a contribution to the study of this phenomenon by investigating the Δ line of a 5d metal. More generally, it represents a further attempt to study the relative contribution of direct transitions and one-dimensional density of states (ODDOS) features to ARP spectra, and to use the direct-transition features to derive $E(\vec{k})$ relations. This latter aspect of ARP has been the subject of numerous studies.[6]

Experimental

The apparatus employed is generally described elsewhere.[1] The base pressure in these experiments was ≤ 3 × 10^{-10} Torr, and the angular acceptance of the CMA was decreased to ±2.5°. The sample was a high-purity (99.99%) Pt crystal (Materials Research Corporation) cut to yield a (100) face, which was diamond-polished to 0.5 μm smoothness and etched briefly in aqua regia. The sample was aligned to better than ±1° using the back-reflection Laue method. Bulk impurities were removed from the sample by repeated cycles of heating in 10^{-6} Torr of O_2 and Ar^+ bombardment, following a procedure described earlier.[7] Cleaning of the crystal was completed _in situ_ by cycles of Ar^+ bombardment followed by annealing at 900°K. After the final cycle, Auger analysis showed impurity (C,O,S) levels of ≤0.05 monolayers. The same procedure, carried out on the same crystal but in a different chamber, yielded a LEED pattern indicative of a reordered 5 × 20 surface, in agreement with previous studies.[8]

The photon source used was the 8° branch line at the Stanford Synchrotron Radiation Laboratory. The geometry of the experiment is shown in Figure 1. Only normal emission spectra were recorded, the angle between the Poynting vector of the incident radiation and the electron propagation direction being 63°. The combined energy resolution (monochromator plus analyzer) varied from ca. 0.1 eV at low photon energies to ca. 0.2 eV at high energies. Spectra were accumulated in 5-10 minutes, and Auger analysis following collection of all spectra showed no increase in contaminant levels.

Results and Discussion

The normal emission ARP spectra of Pt(100) were taken in the range 6 eV $\leqslant h\nu \leqslant$ 32 eV. Representative spectra are shown in Figure 1. The spectra contain features arising from direct transitions and the ODDOS, as well as intensity resonances associated with final-state structure. In order to analyze the direct-transition features in terms of the initial-state dispersion relations, it is first necessary to construct suitable final state(s). The high energy band structure of Pt was not given by Andersen,[9] who reported an RAPW calculation for this metal. However, by analogy with band-structure calculations for palladium[10] and gold,[11] there are three possible final states along Δ in the photon energy range employed here; namely, bands 7, 8, and 9. Only the lowest of these bands will give rise to primary emission, the other two producing emission into a secondary Mahan cone[12] (i.e., involving surface umklapp processes). The character of band 7 is $\vec{G} = (\overline{16},0,0)$, using $\vec{k}$ units of $\pi/4a$, so that for direct transitions, emission arises from final states in the second Brillouin zone. Bands 8 and 9 do not give rise to discernible features in the spectra and will not be considered further.

Previous work on selected low Miller-index faces of Ag,[2,3] Au,[4] and Pt[4] suggests that a quasi-free-electron final state should be used to derive dispersion relations, in place of the bulk final state. This choice is related to the surface sensitivity of photoemission and is most clearly indicated when emission would otherwise be into a gap in the bulk final state. The effective electron mass (m*) of the adopted final state was found in studies of silver and gold by fitting a quasi-free-electron parabola to the calculated bulk final state near the center of the line under investigation. However, by necessity we followed the procedure used for Pt(111)[4] where the effective mass m* was taken to be the value found for the analogous state in gold. Along Δ, a fit to band 7 of gold yields $m^* = 1.4m_e$ where m_e is the free electron mass, the valence-band minimum being adjusted to ($V_0 = -1.4$ eV), which gave the best overall agreement between the empirical valence bands and the RAPW calculation of Andersen.[9] A comparison between the empirical and theoretical valence bands along Δ is shown in Figure 2, and empirical band energies are given in Table 1. As can be seen from Figure 2, for photon energies below 10 eV, the quasi-free-electron final state lies in the first Brillouin zone.

In addition to the direct-transition peaks that yield the data points shown in Figure 2, peaks arising from the density of states (DOS) were also observed. The DOS peak with most intensity occurs at a binding energy of 0.5 eV.

This peak can be seen in the spectra at $19 \text{ eV} \leqslant h\nu \leqslant 32 \text{ eV}$; it is masked at lower photon energies by direct-transition peaks. A weaker DOS feature is observed at a binding energy of 4.0 eV. The relative intensities of both the 0.5 eV and the 4.0 eV peaks increase with photon energy. We interpret this trend as arising from a decrease in the electron mean free path, reducing the extent of $\vec{k}_{\perp}$ conservation and leading to an enhancement of DOS features.[6] The intensities of these DOS peaks are unusually large for Group VIII metals, where direct-transition features have been found to dominate. This probably arises because both the ODDOS and three-dimensional density of states (TDDOS) contribute to its intensity. Although ODDOS features arising from band 4 (Γ_7) and bands 5 and 6 (Γ_8) are not explicitly observed at most photon energies, they do undergo intensity resonances, along with bands 2 and 3, in the photon energy range $17 \text{ eV} \leqslant h\nu \leqslant 22 \text{ eV}$. Resonances were also observed in our ARP study of Pt(111);[4] they were found to arise at photon energies where the bulk final state crosses bands 2-6 near Γ. The resonant maxima in Pt(100) occur at the same photon energies as those observed for Pt(111) (bands (2,3) at 20.5 eV, band 4 at 19.5 eV, and bands (5,6) at 17.5 eV), and occur at the same binding energies (bands (2,3) at 4.1 eV, band 4 at 2.8 eV, and bands (5,6) at 1.4 eV).

Apart from secondary-electron structure, the remaining features in the spectra can be assigned as direct transitions.

Since the radiation incident on the sample was p-polarized, features should be observed from all six initial-state bands.[13] However, band 1 was not observed in our spectra, presumably because of a low cross-section due to its s-p character, although the situation is complicated by the presence of structure in the inelastic tail, similar to that reported by Willis and coworkers[14] for tungsten.

The agreement between the empirical and theoretical band structures, shown in Figure 2, is generally good, although discrepancies are observed. Unfortunately, it is not possible to use symmetry about Γ or X to make a more reliable choice of the final-state valence-band minimum, because of the limited photon energy range available. The major discrepancies are in bands 2, 4, and 5; the lower binding energy of band 4 is also found at Γ from the ODDOS structure at resonance. Band 5 is seen to lie higher than calculated, although it should be noted that for $h\nu \geqslant 20$ eV the positions of peaks associated with this band are difficult to determine. Apart from band 2, which was found to be higher than calculated, the remaining discrepancy is in band 3 between (4,0,0) and (6,0,0), where there is a deviation in the curvature.

It is apparent from our analysis of direct-transition features, shown in Figure 2, that dispersion is observed when emission would correspond to a gap in the bulk final state. Although the exact form of this band is not known, its position at both Γ and X is available. From the final-state resonances observed both in this work and in the spectra of Pt(111), Γ(7) lies 16.5 eV above E_F; the position of X(7) was calculated by Andersen to be 8.9 eV above E_F.

Summary

This communication has described the experimental determination of the platinum valence-band structure between Γ and X by analysis of direct-transition features in the ARP data. Before this could be achieved, features were identified in the spectra arising from the one-dimensional density of states and final-state resonances. The empirical band structure was derived using a quasi-free-electron final state and, as in earlier studies, direct transitions into this state could be assigned even when a gap was present in the bulk conduction-band structure. This study therefore adds further credence to the idea of a surface-modified final state in the analysis of ARP data.

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Table 1

Empirical Band Energies Along Δ In Platinum (eV below E_F)[a]

$\vec{k}(\frac{\pi}{4a})$	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6
0,0,0	-	4.08	4.08	2.8	1.4	1.4
2,0,0	-	4.4	3.8	2.5	1.8	1.35
3,0,0	-	4.6	3.75	2.3	-	1.15
4,0,0	-	4.9	3.4	2.0	1.45	0.9
5,0,0	-	5.2	3.2	-	1.05	0.45
6,0,0	-	5.6	1.6	-	-	-
7,0,0	-	-	0.3	0.5	-	-
8,0,0	-	-	-	0.45	-	-

[a] Error limits are estimated as ±0.07 eV.

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Figure Captions

Figure 1. Selected normal emission spectra of Pt(100) in the photon energy range $11 \leqslant h\nu \leqslant 30$ eV. The inset gives the experimental geometry.

Figure 2. Empirical dispersion relations (circles) and theoretical bands (lines) along Δ for platinum. The scale at the top gives the final state shifted down by the indicated photon energy. The final state crosses from the first to the second Brillouin zone at ca. $h\nu = 11$ eV.

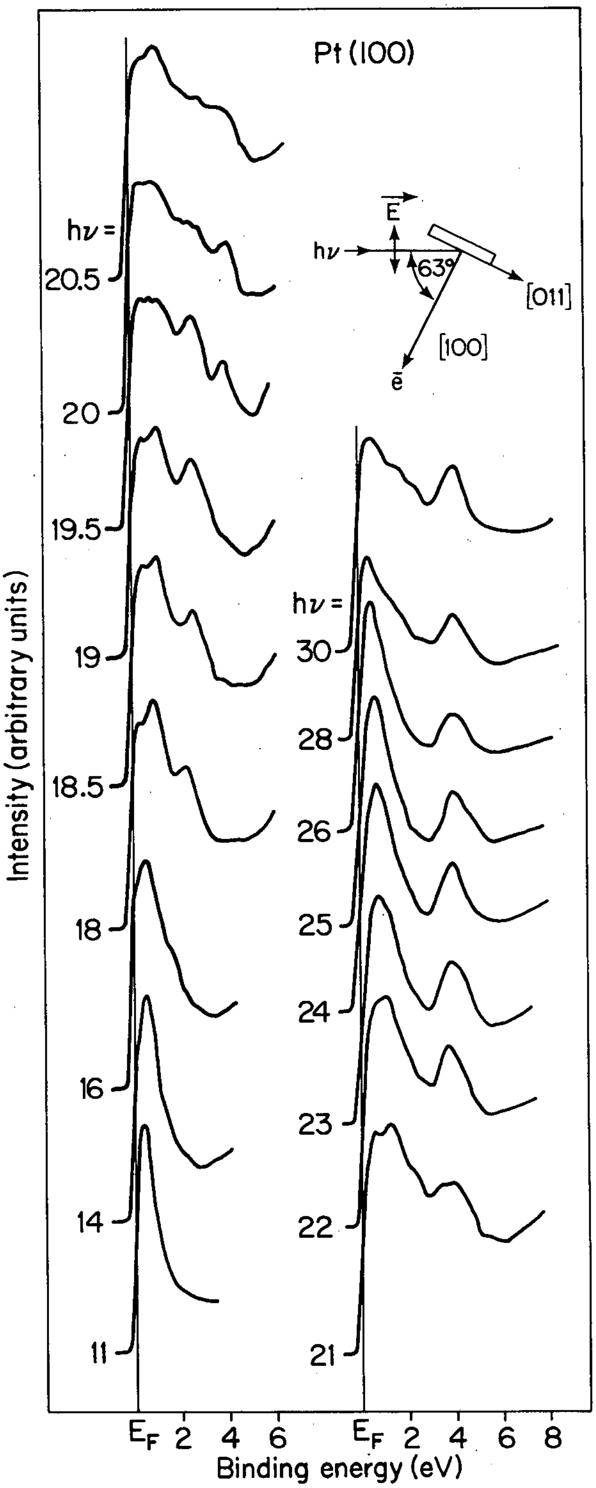

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Figure 1

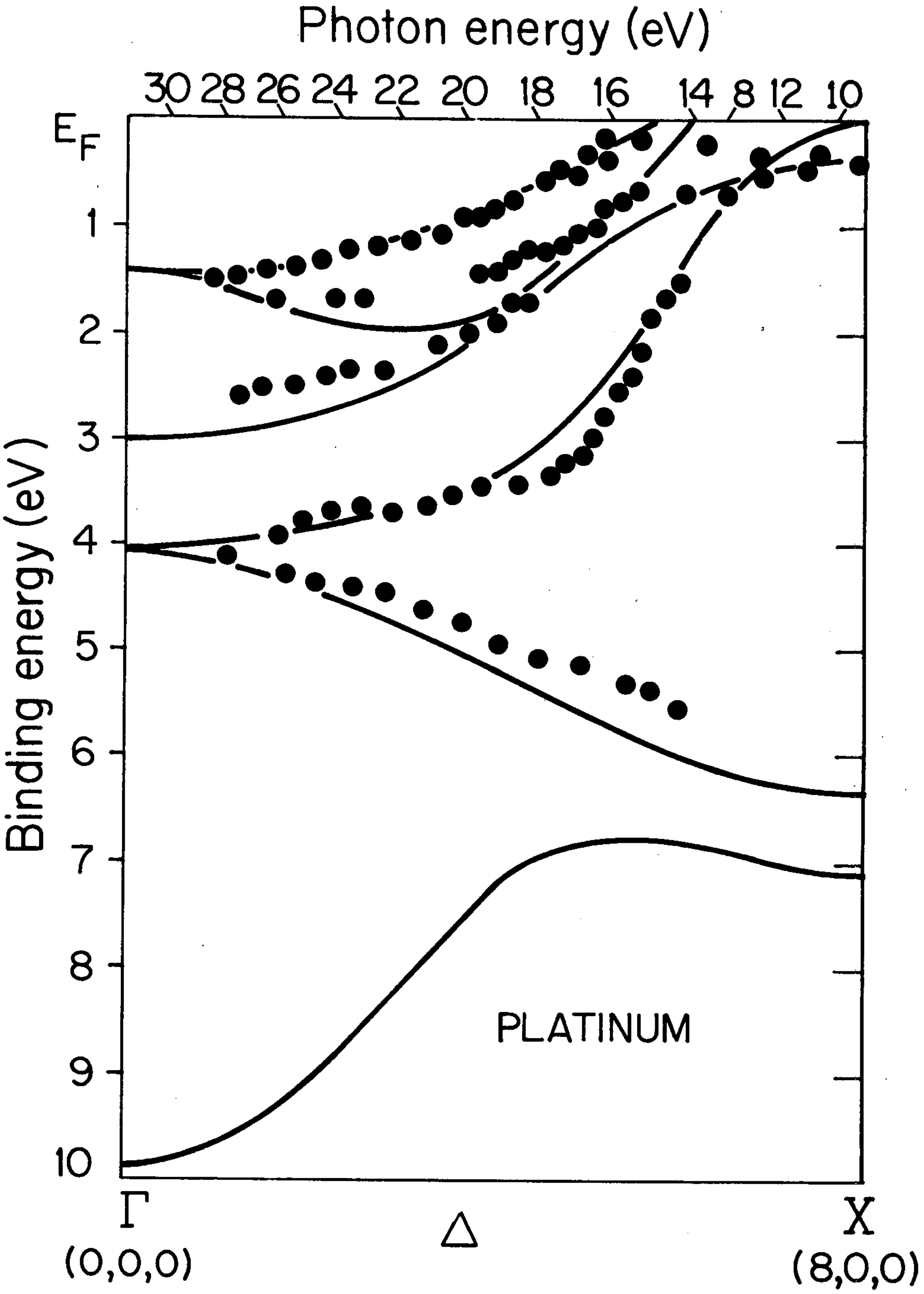

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Figure 2

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