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SPIN-RESOLVED PHOTOEMISSION FROM Pd(1 1 1)

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Circularly polarized synchrotron radiation of BESSY and spin-resolved photoemission have been used for a study of the electronic structure of Pd in Λ-direction The photon energies were chosen between the photoemission threshold at 5 7 and 23 eV We used the highly symmetric experimental setup of normal light incidence and normal photoelectron emission and studied transitions from the two $\Lambda_6^3/\Lambda_{4,5}^3$-band-pairs split by spin-orbit interaction Though the magnitude of the spin-orbit splittings ΔE_{so} in this medium-Z material is smaller than lifetime broadening, it is feasible to resolve the spin-orbit splitting of the initial states via photoelectron spin analysis The data are consistent with a bandstructure calculation of Noffke and Eckardt except for an energy dependent shift of 0 4 to 1 1 eV of the final bands towards higher energies In the occupied part of the bandstructure an avoided crossing could be identified Surface- (bandgap-) emission was observed for photon energies below 7 8 eV

INTRODUCTION

SPIN-RESOLVED PHOTOEMISSION studies with circularly polarized light yielded information about the electronic structure of the high-Z solids Pt [1], Ir [2], and Xe [3] not attainable in a non spin-resolved measurement, namely characterization of the symmetry and information about the hybridization of the states involved in the transitions This work deals with Pd, a medium-Z element, with spin-orbit splittings which, in most cases, are smaller than the principal peak widths due to lifetime broadening A separation of the peaks corresponding to the transitions from spin orbit split initial bands without spin analysis is then only possible employing deconvolution procedures with additional assumptions about the peak shapes The data in this work demonstrate how spin-resolved photoemission can yield detailed information about the bandstructure of a non-magnetic medium-Z material including a resolution of the spin-orbit splitting

EXPERIMENTAL

The experiments were performed at the 6 5 m normal incidence monochromator [4] at BESSY, using an apparatus described previously [1, 5] All data were obtained for normal incidence of the circularly polarized light and with energy as well as spin analysis of the normally emitted electrons The overall energy resolution (electrons plus photons) was better than 250 meV in the photon energy range used (5–23 eV), at an angular resolution of $\pm 3°$

The Pd-crystal surface normal coincided within 0 5° with the [1 1 1]-direction The crystal was held by Pd wires and mounted on top of a liquid He cooled target manipulator For preparation of the clean surface we used Ne^+-bombardment, repeated cycles of heating in oxygen at about 900 K and flashing to about 1300 K The surface was characterized by Auger spectroscopy and LEED, the carbon contamination was determined by thermal desorption spectroscopy of CO, since the carbon signal in the Auger spectrum coincides with a strong Auger emission from Pd [6] Phonon effects were minimized by keeping the crystal at a temperature of about 60 K during the measurements

RESULTS AND DISCUSSION

A typical photoemission spectrum is given in Fig 1 The photoelectron intensity I was obtained for the photon energy $h\nu = 16$ eV and shows a weak and a strong peak As already shown in detail for Ir [2] photo-electron spectra obtained for normal light incidence and normal photo-electron emission can be

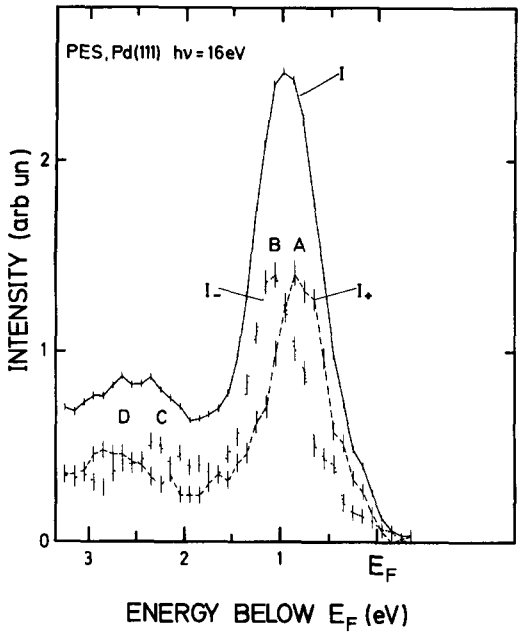

Fig 1 Photoelectron spectrum (PES) for circularly polarized synchrotron radiation at $h\nu = 16$ eV The solid line is the photoelectron intensity I at normal photoemission, which is separated into the partial intensities I_+ and I_- by means of the spin polarization P

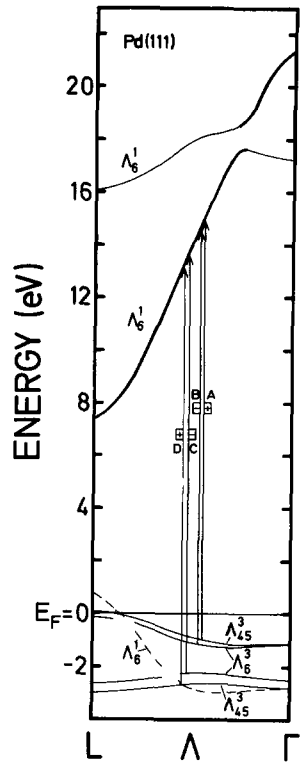

Fig 2 Bandstructure of Pd in the Λ-direction [7] The arrows indicate the transitions into the free electron like final band (heavy line), which are allowed in our geometrical arrangement Transitions from the Λ_6^1-band in the occupied part of the bandstructure (dashed line) are not allowed [8]

separated into parts regarding the symmetry of the initial states involved in the transitions by means of the photoelectron intensity I and spin polarization P according to

$$I_+ = \tfrac{1}{2}I(1 + P) \quad (\Lambda_{4,5}^3\text{-symmetry}),$$

and

$$I_- = \tfrac{1}{2}I(1 - P) \quad (\Lambda_6^3\text{-symmetry})$$

For circularly polarized light with positive helicity (σ^+) I_+ and I_- are the partial intensities with electron spin polarization parallel and antiparallel to the surface normal, respectively They are given as dashed and dotted lines in Fig 1 and demonstrate that both peaks in the total intensity consist of two peaks with different spin polarization When reversing the radiation helicity ($\sigma^+ \rightarrow \sigma^-$), the spin-polarization signs of I_+ and I_- are exchanged

In order to explain this spectrum we regard the bandstructure of Pd in the Λ-direction [7] which is given in Fig 2 In the energy range accessible with our photon energies it consists of 5 bands in the occupied region, whereas in the unoccupied region it shows only a free electron like final band (heavy line) crossed by a flat f-like final band at about 18 eV The crossing is avoided because both bands are of the same Λ_6^1-symmetry type The four arrows in Fig 2 indicate the four transitions allowed for our experimental geometry and the photon energy $h\nu \sim 16$ eV They correspond to the four peaks labelled A, B, C, and D in Fig 1 and yield photoelectrons of both spin-polarization signs as indicated in Fig 2

In the first column of Fig 3 we present a set of photoelectron spectra for photon energies between 6 and 23 eV They may be resolved with regard to the symmetry of the initial states, i e by means of spin-polarization data, they are separated into I_+ and I_- These intensities are given in the second and third column of Fig 3 As general features in these series of spectra one should note

(a) the pronounced peaks corresponding to the transitions A and B for initial energies between 0 and about 1 5 eV below the Fermi level E_F For $h\nu = 9$ eV we observe an intensity decrease and a broadening of the I_- peak B We regard these facts as an experimental evidence for the avoided crossing of the upper Λ_6^3- with the dashed Λ_6^1-band (see Fig 2)

(b) the weak peaks corresponding to the transitions C and D for initial energies between 2 and 3 eV

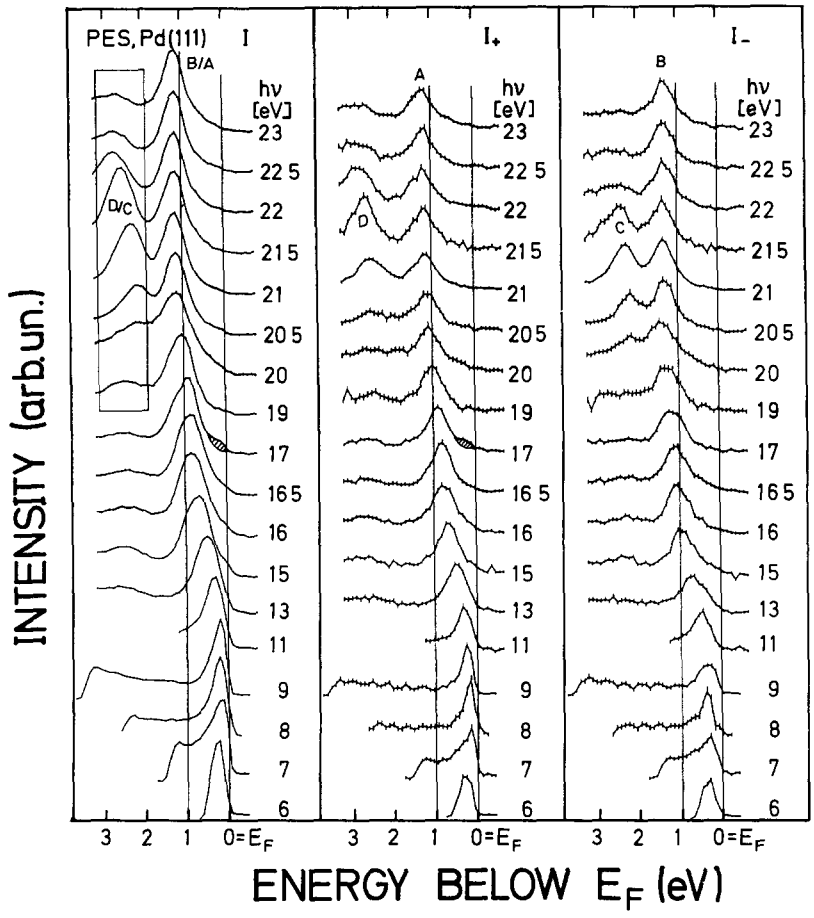

Fig 3 Series of photoelectron spectra for photon energies between 6 and 23 eV The left part shows the total intensities I, the second and third column give the corresponding partial intensities I_+ and I_-, respectively Resonances were studied by constant initial state spectroscopy in the region framed in the first column ($h\nu$ = 19–23 eV) The hatched areas in the spectra for $h\nu$ = 17 eV indicate the emission which is probably due to transitions into the flat f-like band (see text)

These peaks show a resonantly enhanced intensity for photon energies of about 21 eV We studied these resonances more extensively and performed constant initial state spectroscopy in the region framed in the left column of Fig 3, i e at initial energies between 2 and 3 2 eV below E_F and photon energies between 19 and 23 eV Independent of the initial energy the maximum photoelectron intensity is obtained for the final energy 18 8 eV This is true for the total intensity I as well as for I_+ and I_- The maximum intensity vs initial energy is obtained for 2 2 and 2 6 eV below E_F for I_- and for I_+, respectively All these findings are in agreement with the interpretations of Wern *et al* [9], who found similar resonances for Ag and attributed them to transitions into the bent region of the first unoccupied band where the free electron like band meets the short part of the f-like final band near Γ

(c) the photoelectron intensity increase just below E_F for $h\nu$ = 17 eV (shaded area in Fig 3) The increase is only due to electrons with positive spin polarization and probably corresponds to transitions from the highest occupied $\Lambda^3_{4,5}$-band into the flat f-like final band These transitions have also been observed for Ir [2]

The spectra in Fig 3 are normalized to the first peak (A/B) in the total intensity An absolute normalization to the photon flux yields variations up to a factor 3 with maxima at about 15 and 23 eV, minima are obtained for energies below $h\nu$ = 10 eV and at $h\nu$ = 20 eV The spin-orbit splitting in the spectrum (i e the difference between I^+ and I^-) for $h\nu$ = 23 eV disappears and indicates that the corresponding transition occurs near Γ The minimum at $h\nu$ = 20 eV is caused by the gap occurring as a consequence of the avoided crossing in the unoccupied part of the band-structure

In addition to the results presented we also performed measurements without spin analysis in the whole

photon energy range and at some higher energies From these data we obtained steplike constant kinetic energy features with steps occurring at 7 8 ± 0 3 eV and at 18 5 ± 0 3 eV These are secondary electron emissions from points of high density-of-states in the unoccupied part of the bandstructure [10] and are used together with other findings mentioned above to determine the bandstructure of Pd(1 1 1) in the Λ-direction experimentally Like Himpsel and Eastman (H + E) [10] we proceed in two steps First, we collect information about critical points of the final bands and use a calculated bandstructure to interpolate between these points Secondly, we regard these bands as experimentally verified final bands and perform a bandmapping procedure to obtain the initial bands using the spin-resolved photoemission data of Fig 3 Apart from the secondary electron emissions we regard the peak at $h\nu$ = 17 eV, the resonances at final energy 18 8 eV and the absolute peak maximum at 23 eV as critical points of the unoccupied part of the bandstructure These points are given in Fig 4 and are compared with a bandstructure calculation of Noffke and Eckardt (N + E) [7] It is obvious that a shift of the calculated unoccupied bands by 1 1 ± 0 3 eV yields a good fit to the experimental results except for the critical point at 7 8 eV final energy For the bandmapping of the occupied bands we therefore use N + E's bands and modify them with an energy dependent shift towards higher energies At energies between 16 and 22 eV they are shifted by 1 1 eV, at lower energies we choose a shift decreasing continuously from 1 1 to 0 4 eV in order to obtain agreement with the point at 7 8 eV These shifted bands and the resulting bandmapping points are also given in Fig 4 We attribute the shift to self energy corrections [11–13] The direction, the energy-dependence and the size of the shift support this assumption The mapping points are compared with N + E's calculation [7] and show good agreement except for slight deviations occurring far from Γ and L One should note that these differences would decrease or even vanish if we assume larger values of the self energy corrections between 12 and 16 eV final energy Such abrupt increases of the self energy correction values with final energy have already been proposed theoretically by Williams and v Barth [12] and experimentally been found by Speier *et al* [13] A further slight discrepancy is a fact which has already been found experimentally earlier in [10, 14] Near L the $\Lambda^3_{4\,5}$ band lies below the Fermi level, while different calculations give it slightly above E_F [7, 15, 16] Comparing our data with those of the non spin resolved study of [10] we find a discrepancy in the size of the spin-orbit splitting for the upper occupied bands While H + E found a maxi-

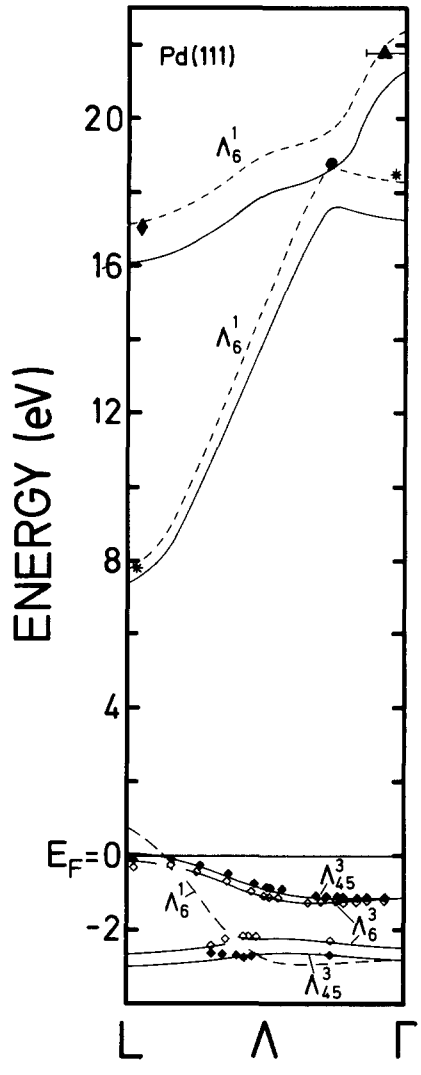

Fig 4 Bandstructure determination of Pd in the Λ-direction in two steps First step· determination of critical points of the band-structure and interpolation of these points with calculated bands from [7] Critical points * secondary electron emissions, ● resonance (see text), ♦ transition into flat *f*-like band near L, ▲ maximum of the absolute intensity for $h\nu$ = 23 eV For a good agreement of the critical points with theory the calculated unoccupied bands (solid) [7] have to be shifted by an energy dependent value between 0 4 and 1 1 eV towards higher energies (dashed curves) Second step spin-resolved bandmapping of the occupied part of the bandstructure using these shifted final bands (dashed) and the experimental spin-resolved PES ◆ mapping points for bands with $\Lambda^3_{4,5}$ symmetry ◇ mapping points for bands with Λ^3_6 symmetry The lines in the occupied part of the bandstructure represent the bandstructure calculation [7], dashed lines indicate Λ^1_6 symmetry, dotted lines avoided crossings of Λ^3_6- and Λ^1_6-bands and solid curves the bands Λ^3_6 and $\Lambda^3_{4\,5}$

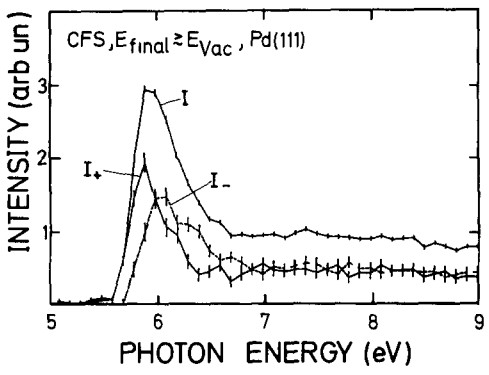

Fig 5 Constant final state spectrum (CFS) for a final energy just above the vacuum level The total intensity I is separated into I_+ and I_- with regard to the spin-polarization sign of electrons for σ^+-light and thus the symmetry of the initial states The peak is due to surface emission (see text)

mum value of 0 4 eV, our splitting values are not larger than 0 25 eV, this difference is probably based upon the peak separation procedures used For the lower bands we find a splitting of 0 4 $\pm$ 0 1 eV, which could not be determined in [10] because of the overlap with emission from $\Lambda_6^1 \rightarrow \Lambda_6^1$ transitions and large lifetime broadening values compared to the splitting

As given in Fig 3 we also find emissions for photon energies below 7 8 eV, where the calculation [7] as well as several other calculations [15–17] performed for an infinitely extended crystal yield a bandgap While the data in Fig 3 show that these emissions to the bandgap region are found for photon energies between 6 and 8 eV, Fig 5 is a constant final state spectrum (CFS) with final energy just above the vacuum level This spectrum is also resolved with regard to the symmetries of the initial states and shows that the emission of I_+ starts at 150 meV lower photon energies than that of I_- As these emissions also strongly depend on surface contaminations we think that they are due to transitions into evanescent states [18, 19], i e states which are solutions of a complex bandstructure calculation and decrease exponentially from the crystal surface into the bulk

SUMMARY

We studied the bandstructure of Pd in Λ-direction by means of spin-resolved photoemission The spectra could be resolved with regard to the symmetry of the initial states, though the spin-orbit splittings of this medium Z material are smaller than lifetime broadening in most cases The data yield information about hybridization, an avoided crossing in the occupied part of the bandstructure could be identified and critical points in the unoccupied part of the band- structure were determined These points are in good agreement with calculations of Noffke and Eckardt except for an energy dependent shift between 0 4 and 1 1 eV towards higher energies As in [2] this shift is assumed to be due to self energy corrections A bandmapping of the occupied bands performed with these shifted final bands yielded also good agreement with the calculation of Noffke and Eckardt with the exception of a slight but fundamental discrepancy at L Bandgap-(surface-) emission was observed for photon energies below 7 8 eV

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