PHYSICAL REVIEW B VOLUME 19, NUMBER 12 15 JUNE 1979

Ultraviolet photoemission from Pd(111)

N. Dahlbäck and P. O. Nilsson
Department of Physics, Chalmers University of Technology, S-402 20 Gothenburg, Sweden

M. Pessa
Department of Electrical Engineering, Tampere University of Technology, SF-33101 Tampere 10, Finland
(Received 20 November 1978)

Angular-resolved photoemission from Pd(111) has been measured in the photon energy range of 12–41 eV. The results have been analyzed in terms of direct optical transitions in the bulk band structure.

I. INTRODUCTION

The electronic structure of palladium has been the subject of a number of recent papers.[1-6] However, only a few detailed experimental studies of the band structure of Pd throughout the entire energy range of the valence band have so far been published. Traum and Smith[4] used an angle-integrated photoemission technique to study the electronic structure of polycrystalline Pd films. Smith[3] found agreement between observed features in the energy distribution curves and calculated features in the joint density of states. More detailed information about the band structure is obtainable if angle-resolved photoemission of single crystals can be measured. Such measurements on Pd have recently been carried out by Lloyd *et al.*[6] Contrary to Smith,[3] their interpretation of the data was based solely upon a one-dimensional density of occupied states which may be too crude an approximation for understanding the low-energy photoemission of palladium.

We have made an attempt to perform a systematic analysis of angle-resolved photoemission of a Pd(111) single crystal. Results of our measurements and an interpretation of the data are presented in this paper.

II. EXPERIMENT

A palladium single crystal was cut along the (111) face and was oriented to an accuracy of better than 1°, as deduced from Laue diffraction patterns. Prior to introducing the sample into the ultrahigh vacuum (UHV) chamber the surface was polished mechanically and electrochemically. In the UHV chamber the sample was further cleaned by repeated cycles of 500-eV argon ion bombardment and heating at 800 K. The azimuthal orientation was checked by studying LEED patterns to make sure that a desired symmetry plane of the crystal coincided with the plane defined by the uv light beam, crystal, and the analyzer.

The light source was a gas-discharge lamp which produced all the usual rare-gas resonance lines between $\hbar\omega = 11.85$ eV (Ar I) and 40.8 (He II). The analyzer was a preretarding cylindrical condenser having an energy resolution of about 0.2 eV and an electron acceptance cone of 3° full opening. The angle of incidence of the uv light and the emission angle of electrons could be varied independently. The base pressure in the UHV chamber was 1×10^{-10} Torr, and the working pressure with the gas lamp on was 2×10^{-9} Torr.

III. THEORY

In the present calculation we have applied the three-step model of photoemission which assumes that three independent processes take place. These are: (i) an excitation from an initial state to a final state through a direct optical transition, (ii) an electron transport to the surface, and (iii) an escape through the surface with a probability which is dependent on kinetic energy and the direction of propagation. This model has been successfully used in the analysis of peak positions in the energy distribution curves of photoemission of, e.g., noble metals.[7-10] Transition matrix elements are taken to be constant throughout the valence band. This assumption is a crude approximation when peak intensitites are considered but it does not in general influence peak positions which are the prime interest for our study of the electronic band structure. Additional structure, arising from surface states and resonances, are observed for some materials[10-12] and even dominate the spectra in some cases.[13] As will be seen here these effects are not observed for palladium. Other mechanisms not included here, such as surface-induced photoemission, have been suggested to be responsible for the appearance of strong features in spectra of transition[14,15] and noble metals.[16]

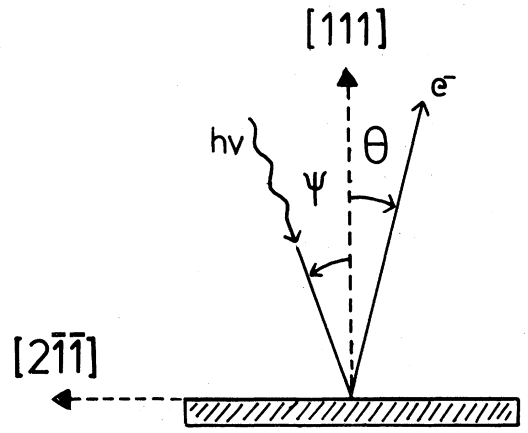

FIG. 1. Experimental configuration. $\hbar\omega$: incident photons, e^- : emitted electrons.

IV. RESULTS

The incident angle of photons Ψ and the electron detection polar angle θ are defined in Fig. 1. Both of them are in the azimuthal plane (0$\bar{1}$1) which corresponds to the Γ LUX plane in the Brillouin zone. For each photon energy two sets of energy distribution curves were recorded by varying the emission angle, namely, one for $\Psi = 35°$ and another for $\Psi = 60°$. In the former case θ varied between 0° and 45° and in the latter case between −25° and +25°. Only the results for two photon energies are presented here, viz., Ne I (16.8 eV) and He I (21.2 eV). These results are shown in Figs. 2–5.

The energy-distribution curves are characterized by a strong emission region from the Fermi level ($E = 0$) down to about 4 eV below the Fermi level. The structure corresponds to emission

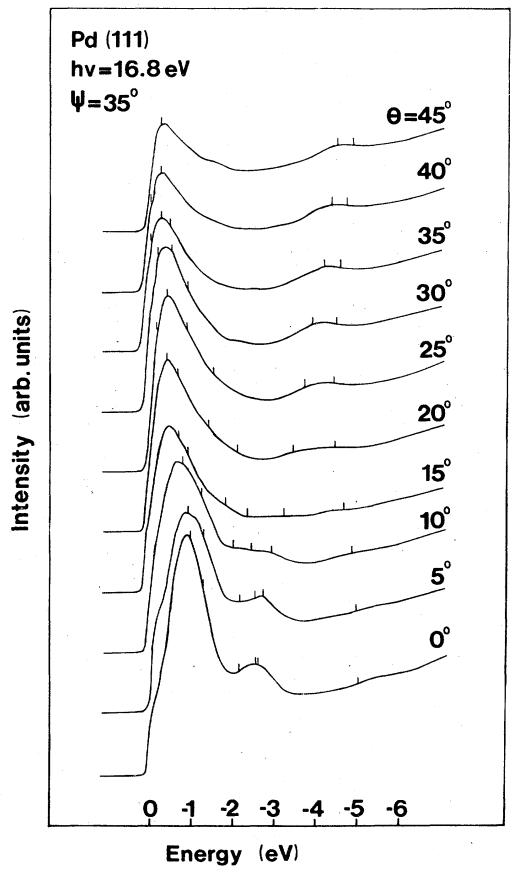

FIG. 2. Experimental energy distribution curves (EDC's) of photoelectrons. The angles θ and ψ are defined in Fig. 1. The vertical bars show the energy positions where interband transitions could contribute according to the theory. The photon flux for the different emission angles was the same.

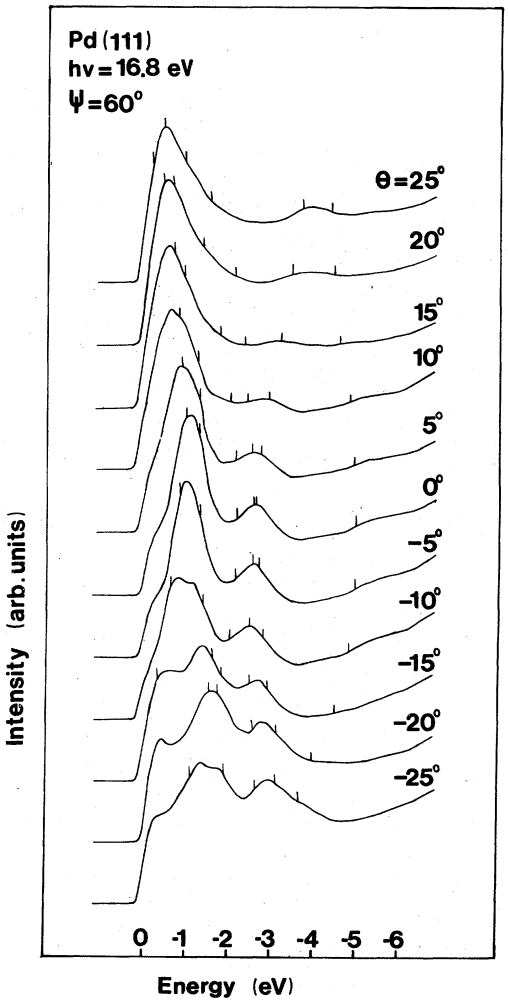

FIG. 3. As for Fig. 2 but with other parameters.

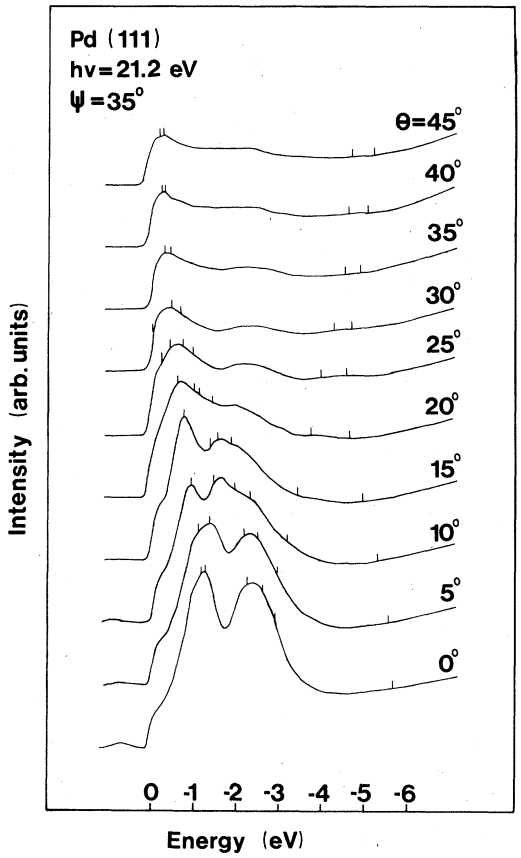

FIG. 4. As for Fig. 2 but with other parameters.

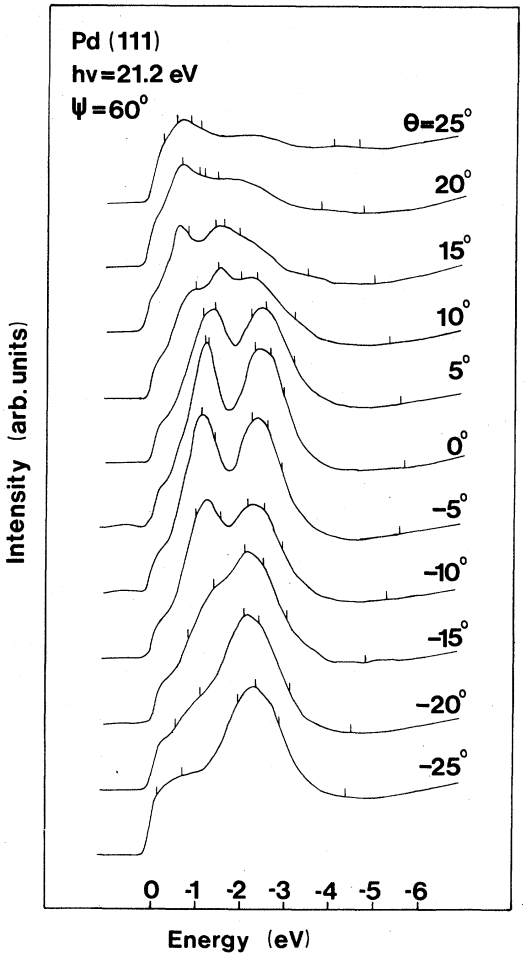

FIG. 5. As for Fig. 2 but with other parameters.

from the nearly filled $4d$ band. Another immediate observation is that the overall profile of the curves varies strongly as a function of emission angle.

Comparison of our spectra with those obtained by Lloyd *et al.*[6] shows that an agreement is obtained only for emission normal to the (111) face (Γ-L direction, $\theta=0$, $k_{\parallel}=0$), and appreciable differences occur for off-normal emission. For example, at a photon energy of 16.8 eV and $\theta=-20°$ we observe a feature at −2.8 eV, Fig. 3, while Lloyd *et al.* find a structure around −4 eV.

As shown in Figs. 2–5, a change in Ψ only slightly modified the amplitudes of the peaks. Perhaps the most pronounced effect occurs for normal emission at $h\nu=16.8$ eV; when $\Psi=35°$ the intensity ratio of the two strong peaks is 2.6 while for $\Psi=60°$ the ratio is 2.0.

Strong variations in peak positions can be observed as the photon energy is varied (Fig. 6). This fact indicates that the $\vec{k}$ conserving selection rule is important for the studied transitions. Thus the effect excludes a dominant contribution of surface-induced emission.[15]

V. DISCUSSION

In the calculations the final-state band was represented by a free-electron parabola. Because of the damping effect the free-electron band may sometimes be a better approximation[17] for an excited electron than an actual calculated bulk band of the ground state. However, in our case the assumption of a free-electron final state is hardly critical since the actual bulk bands also have a parabolic form in the energy range under study. The bottom of the fitted parabola was found to lie at 2.7 eV below the Fermi level.

For the initial states we have used the band structure obtained by Pessa *et al.*[18] They used the Hodges-Ehrenreich-Lang interpolation scheme in the form refined by Smith and Mattheiss[19] and found a good agreement with relativistic aug-

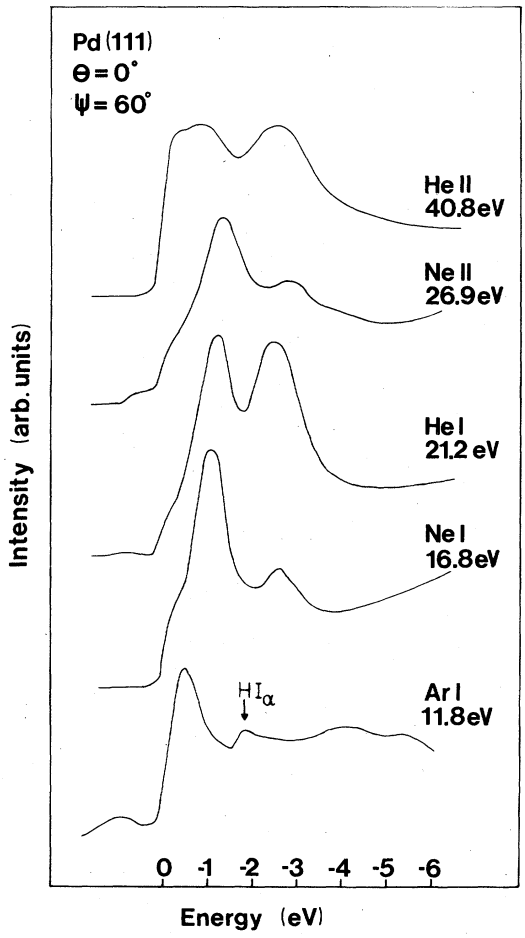

FIG. 6. Experimental EDC's for normal emission ($\theta = 0$) for different photon energies. The angle ψ is defined in Fig. 1.

mented plane wave bands calculated by Christensen.[20]

Experimental and theoretical results are summarized in Figs. 7 and 8 where experimental peak positions of the spectra in Figs. 2–5 are compared with calculated peak positions as a function of θ. Since the final state is always the same band the six calculated lines represent the six initial states. Here we have assumed (solid lines) that the features arise mainly from "primary cone emission," i.e., only $\vec{g} = (111)$ is involved in excitation and transport processes.

The calculated peak positions are also marked on the measured energy distribution curves in Figs. 2–5. Some of the calculated peaks can be clearly identified with structures in the measured curves. All of the clearly resolved experimental structures have been marked with their energy positions in the structure plots. In this way it is

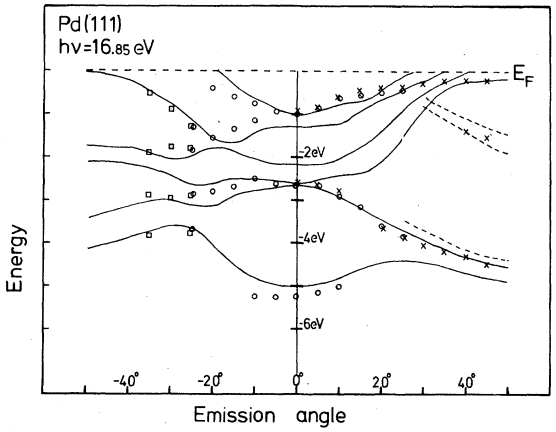

FIG. 7. Structure plot for $\hbar\omega = 16.8$ eV. The solid lines are the theoretical peak positions shown as a function of θ for different band pairs. The symbols X, 0, □ show the energy positions of well-resolved structures in experimental EDC's. Note that the experimental peak can be a sum of two or more transitions. The dashed lines show calculated peak positions for the second, third, and fourth bands for the most probable secondary cone emission.

possible to verify parts of the calculated band structure. By the present technique of varying the detection angle for constant photon energy the band structure is probed along certain curved lines in $\vec{k}$ space. As can be observed, the agreement lies within the experimental uncertainty. Possibly the lowest calculated s-p-like band is a few tenths of an eV too high in energy. In the region from the Fermi level and 1 eV below it is not possible to make a detailed comparison because the cutoff of the Fermi level distorts the peaks. Transitions from some of the initial

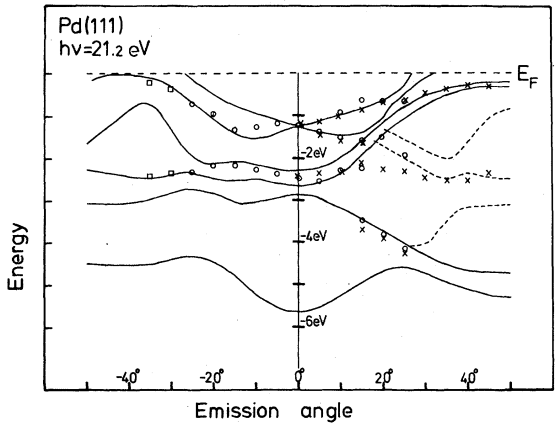

FIG. 8. Structure plot for $\hbar\omega = 21.2$ eV. Notations as given in text of Fig. 7.

bands are very weak or are not seen at all. This can be attributed to low transition probabilities which are sometimes combined with overlapping between two or several peaks.

For large positive values of θ (>45°) a band gap opens up in the structure plots of Figs. 7 and 8 so that no primary emission is expected to occur between band 3 near the Fermi edge and bands 1 and 2 which are situated below −4 eV. However, a weak structure appears around −2.5 eV. To identify this structure we have considered the possible occurrence of "secondary cone emission"[10] due to higher Fourier components of the final Bloch function whose $\vec{g}$ vectors are not involved in the optical transition. In Figs. 7 and 8 the dotted lines indicate peak positions originating from "secondary cone emission" from the bands 2, 3, and 4 with $\vec{g}=(200)$. According to this analysis, the observed features around −2.5 eV result from the (111) component of the Bloch wave. Hence, when primary and secondary cone emission is taken into account all the main features in the measured spectra can be related to properties of the bulk band structure.

Hermansson[21] has shown that strict selection rules in the matrix element apply for certain geometries of a photoemission experiment in the nonrelativistic case. In particular, for emission normal to the surface, and also for a mirror plane, only certain initial symmetries are allowed for a given polarization of the incident light. In the present case we have performed a group theoretical analysis and have realized that, due to the mixing of symmetries by the spin-orbit interaction, no such rules are valid in the mirror plane. For normal emission some selection rules do exist but the required experimental configurations could not be arranged. In the present set up it is necessary to have light polarized perpendicular to the mirror plane. Alternatively, unpolarized light can be used if the angle of incidence is in a plane perpendicular to the mirror plane. Our finding of no selection rules in the matrix element for the present experiment is supported by the fact that, on varying the angle of light incidence in the mirror plane, the observed intensity variation of peaks is relatively small.

Recently, Louie[22] has presented calculations on surface states on the Pd(111) face. From these it can be found that, e.g., in normal emission, three of the predicted surface states might be observable. One state should appear just below the Fermi level, and the others at −2 and −4 eV, respectively. However, from Fig. 6 we conclude that no prominant features are observed in the spectra at these energies. Also for non-normal emission no clear evidence for surface states can be found in the curves.

Photoemission from surface states of other metals has been reported in literature. For instance, for the noble metals strong emission from a surface state just below the Fermi level is well established.[10,11,17,23] However, the corresponding s-p-like state for Pd occurs 2 eV above the Fermi level, and is thus not accessible with the photoemission technique.

It is not clear why the calculated[22] d-like surface states are not observed in the present data. The analysis is complicated by the fact that strong hole damping occurs giving rise to broad structures. Further the surface states are expected to overlap with interband transitions.

It should also be mentioned that Lloyd *et al.*[6] did observe some surface sensitive structures, which they tentatively associated with surface resonances.

ACKNOWLEDGMENTS

We wish to thank Dr. J. Kanski for several valuable discussions. We also wish to express our gratitude to Professor G. Brogren for his continuous interest and encouragement. The work is supported by grants from the Swedish Natural Science Research Council.

[1]J. F. Janak, D. E. Eastman, and A. R. Williams, Solid State Commun. 8, 271 (1970).
[2]F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdynn, Phys. Rev. B 1, 4617 (1970).
[3]N. V. Smith, Phys. Rev. B 9, 1365 (1974).
[4]M. M. Traum and N. V. Smith, Phys. Rev. B 9, 1353 (1974).
[5]A. Y-C. Yu and W. E. Spicer, Phys. Rev. 169, 497 (1968).
[6]D. R. Lloyd, C. M. Quinn, and N. V. Richardson, Surf. Sci. 63, 174 (1977).
[7]P. O. Nilsson and L. Ilver, in *Proceedings of an International Symposium on Photoemission* (ESA Scientific and Technical Publication Branch ESTEC, Noordwijk, Netherlands, 1976).
[8]E. Dietz, H. Becker, and U. Gerhardt, Phys. Rev. Lett. 36, 1397 (1976).
[9]L. Ilver and P. O. Nilsson, Solid State Commun. 18, 677 (1976).
[10]G. V. Hansson and S. A. Flodström, Phys. Rev. B 17, 473 (1978); thesis (Linköping University, 1978) (unpublished).
[11]P. O. Gartland and B. J. Slagsvold, Phys. Rev. B 12, 4047 (1975).
[12]Shang-Lin Weng, T. Gustafsson, and E. W. Plummer,

Phys. Rev. Lett. 39, 822 (1977).
[13]G. V. Hansson and S. A. Flodström, Phys. Rev. B 18, 1562 (1978).
[14]B. Feuerbacker and N. E. Christensen, Phys. Rev. B 10, 2373 (1974).
[15]B. Feuerbacher and R. F. Willis, J. Phys. C 9, 169 (1976).
[16]P. Heinemann, H. Neddermeyer, and H. F. Roloff, Phys. Rev. Lett. 37, 775 (1976).
[17]P. O. Nilsson and N. Dahlbäck, Solid State Commun. 29, 303 (1979).
[18]M. Pessa, M. Lindroos, P. Heimann, and M. Lähdeniemi, Research report No. 24 (1977), Dept. of Physics, Tampere University (unpublished).
[19]N. V. Smith and L. F. Mattheiss, Phys. Rev. B 9, 1341 (1974).
[20]N. E. Christensen, Phys. Rev. B 14, 3446 (1976).
[21]J. Hermansson, Solid State Commun. 22, 9 (1977).
[22]S. G. Louie, Phys. Rev. Lett. 40, 1525 (1978).
[23]P. Heimann, H. Neddermeyer, and H. F. Roloff, J. Phys. C 10, L17 (1977).