Characterization of Symmetry Properties of Pt(111) Electron Bands by Means of Angle-, Energy-, and Spin-Resolved Photoemission with Circularly Polarized Synchrotron Radiation

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An angle-, energy-, and spin-resolved photoemission experiment has been performed for Pt(111) with the circularly polarized synchrotron radiation of the new German dedicated storage ring BESSY. The photoelectron polarization measured as function of the kinetic energy at different photon energies between 6.5 and 24 eV for normal incidence and normal emission shows a pronounced spectral variation up to ±55%. The electron intensities and polarizations observed allow a symmetry-resolved band characterization of Pt in the Γ-L direction.

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Spin-polarized photoelectrons obtained in photoemission from unpolarized targets using circularly polarized light are a very common phenomenon in atomic and molecular[1] as well as solid-state[2] physics. This type of measurement in photoemission from nonmagnetic solids was, however, up to now restricted to angle-integrated studies and to the photon energy range below 10 eV. With development of the storage ring BESSY a light source with sufficiently high intensity of circularly polarized vacuum ultraviolet radiation has become available, which makes angle-, energy-, and spin-resolved photoemission studies even in a photon energy range > 10 eV feasible.

It is the purpose of this Letter to report the first measurements performed on Pt(111) in normal incidence and normal emission in the photon energy range between 6.5 and 24 eV. Opposite to the angle-resolved photoemission from magnetic solids[3] in which the photoelectron polarization is primarily an effect of the initial states, in the photoemission from nonmagnetic solids using circularly polarized radiation, the spin polarization is induced by the selection rules for the quantum numbers for direct dipole transitions. The spin-polarization results measured are discussed in terms of symmetry properties[4] of bands in application of group theory.

We briefly discuss the main components of the apparatus (Fig. 1). The synchrotron radiation is dispersed by a 6.5-m N.I. UHV monochromator of the Gillieson type,[5] not shown in Fig. 1. The bandwidth of the radiation was 0.7 nm. Apertures movable in the vertical direction are used to select radiation emitted above or below the storage-ring plane, which has positive or negative helicity, respectively. The photoelectron–spin-polarization studies have been performed with a degree of circular polarization of $P_{\text{circ}} = \pm(92 \pm 1)\%$,[6] corresponding to a vertical angular range from ±1 to ±5 mrad. Under these conditions a photon flux of the order of 10^{11} s^{-1} (200 mA beam current) passed the monochromator exit slit.

The elliptically polarized light hits the Pt(111) crystal under normal incidence. The sample is cleaned by ion bombardment, heating in oxygen,

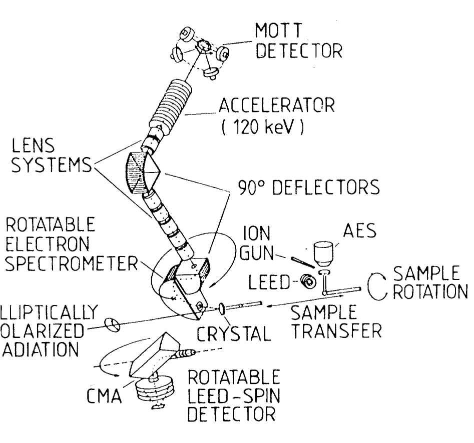

FIG. 1. Schematic diagram of the apparatus shown for the general case of off-normal photoemission.

and flashing; it is characterized by low-energy electron diffraction (LEED) and Auger-electron spectroscopy in a separate preparation chamber. The photoelectrons are analyzed with respect to their kinetic energy either by a cylindrical-mirror analyzer followed by a LEED spin detector[7] or by a simulated hemispherical spectrometer[8] followed by a UHV Mott detector.[9] Both electron spectrometers, which are movable up and down into the measuring or waiting position, are rotatable about two different axes which are perpendicular to the photon momentum at the crystal. These rotation axes being different with respect to the light-polarization ellipse will become important in future studies of off-normal photoemission, so that both spin analyzers, shown in Fig. 1, will complement each other, whereas in the normal photoemission discussed in this Letter both methods indeed give the same results within the experimental uncertainties.

In the upper system shown in Fig. 1 the photoelectrons analyzed with respect to their kinetic energy are directed by an electrostatic deflection by 90° along the axis of rotation of the electron spectrometer. After a second deflection they are accelerated to 120 keV and scattered at the gold foil of the Mott detector. The spin polarization has been measured by two pairs of detectors as shown in Fig. 1 and has been found to be aligned with the photon momentum. Instrumental asymmetries have been eliminated by taking advantage of the reversal of the light helicity (typically each minute) as well as by use of four additional detectors in forward scattering directions[9] in the Mott detector (not shown in Fig. 1). Typical count rates in the surface barrier detectors of the Mott detector were 10^2 to $10^3\ \mathrm{s}^{-1}$. The energy-dependent energy and angular resolution of the system was 300–450 meV and $\pm(3\text{–}4)^\circ$, respectively.

Pt(111) was chosen because of its high atomic number and its unreconstructed surface. The non-self-consistent fully relativistic augmented-plane-wave (RAPW) band structure of Anderson[10] has been extended to energies up to 22 eV above the Fermi level E_F as shown in Fig. 2. In the following the symmetry properties of the bands along the Λ direction in $\vec{k}$ space are used, which we number at L from 1 to 10 with increasing energy. In normal emission the dominant direct ion interband transitions are these occurring from the initial d bands Nos. 2–6, with symmetries Λ^3_{4+5}, Λ^3_6, Λ^1_6, Λ^3_6, Λ^3_{4+5}, to the totally symmetric final-state band No. 7 of type Λ^1_6. For normally incident light the initial states Λ^3_{4+5}, Λ^3_6 which evolve from the two nonrelativistic Λ_3 doublets of the d-band complex will give the most intense contribution, since a transition $\Lambda^1_6 \rightarrow \Lambda^1_6$ is forbidden in that geometry. Thus four direct transitions from those initial d bands shown as solid lines in Fig. 2 are expected to occur.

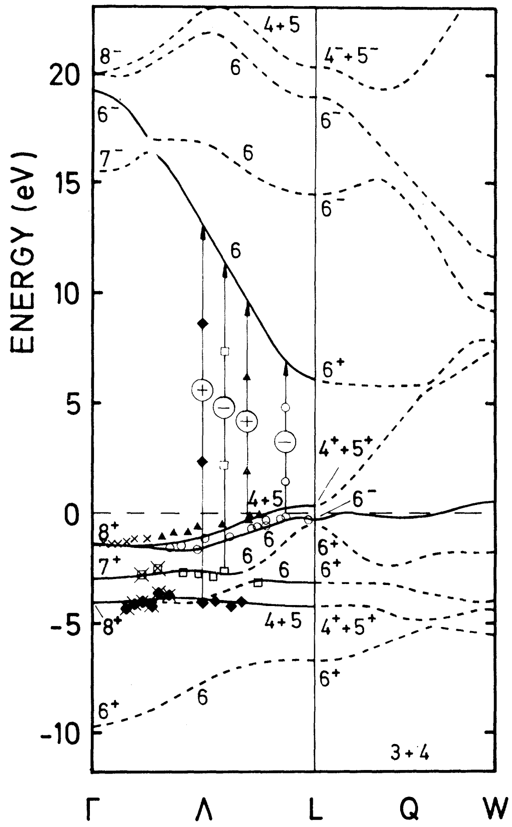

FIG. 2. Symmetry-resolved band mapping of Pt (Ref. 11) in comparison with the calculated band structure: the band mapping procedure used the calculated final band No. 7 for photon energies < 20 eV and a free-electron parabola (not shown) with $V_0 = -1.85$ eV and $m^* = 1.10 m_e$ for $h\nu > 20$ eV, which yields the mapping points without and with crosses, respectively. The mapping points (filled for positive polarization and open for negative) have been obtained by a combination of the intensity and spin-polarization results, partly shown in Fig. 3.

Some examples of experimental photoelectron energy distribution curves (EDC) and corresponding electron spin polarizations (ESP), measured at nineteen different photon energies, are presented in Fig. 3. The ESP values are normalized to a complete circular polarization with positive helicity (photon spin and momentum parallel). The electron spin is quantized along the surface normal which defines the z axis. The selection rules for the production of spin-polarized electrons in cubic crystals as given in Ref. 4 have predicted a positive

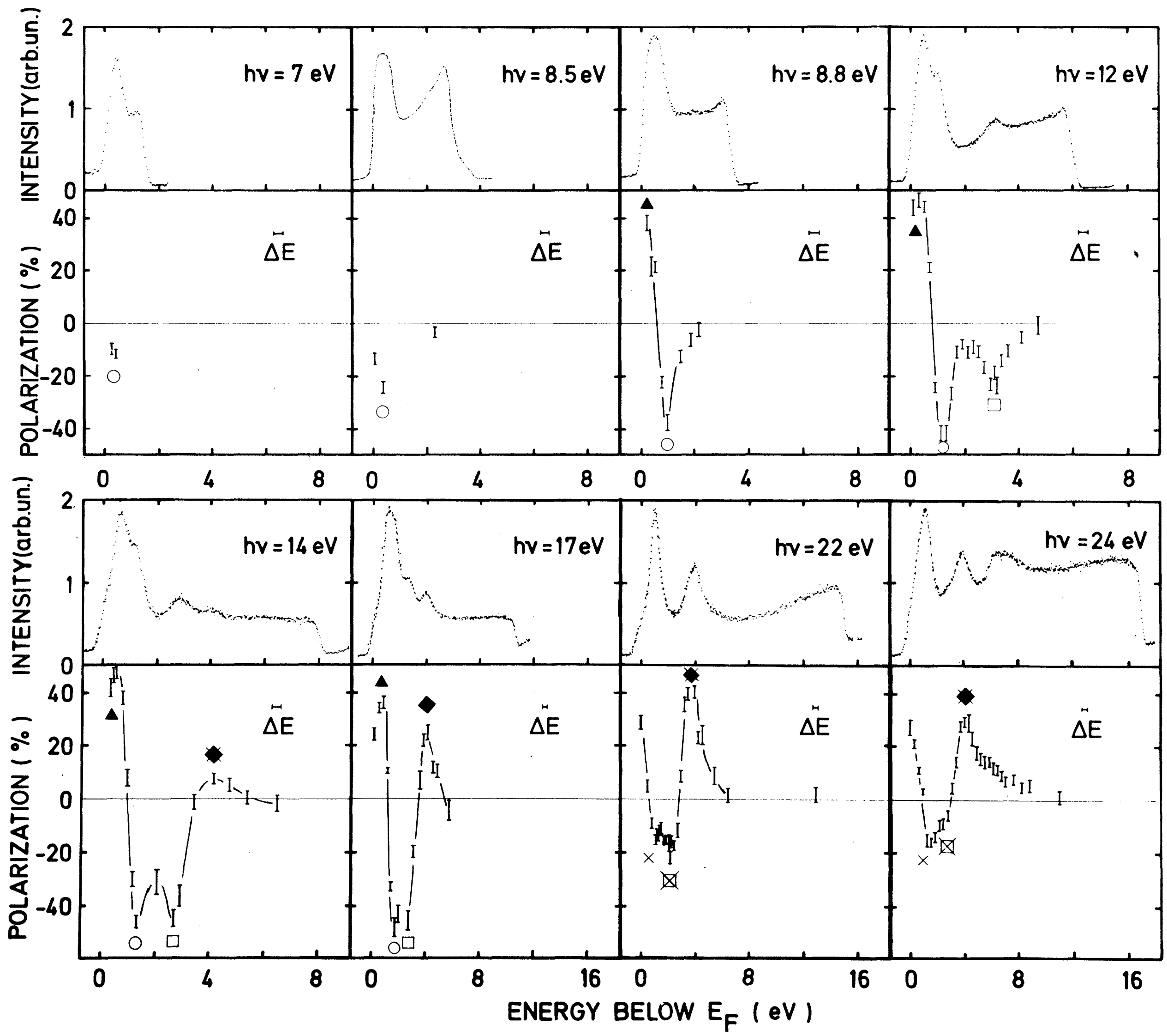

FIG. 3. Photoelectron EDC's (with respect to the Fermi energy E_F) of Pt(111) (upper parts) and corresponding spin-polarization results (lower parts) for normal incidence and normal photoemission using circularly polarized synchrotron radiation (intensities are not normalized). The error bars contain the statistical error (one standard deviation) of the spin-polarization measurements of photoelectrons (typically $\Delta P = \pm 0.02$) and photons ($\Delta P = \pm 0.01$) as well as the uncertainty of the asymmetry function (0.26 ± 0.01) of the Mott detector. The symbols at the polarization peaks correspond to those in Fig. 2.

(negative) ESP for a transition of type $\Lambda^3_{4+5} \rightarrow \Lambda^1_6$ ($\Lambda^3_6 \rightarrow \Lambda^1_6$).

According to Fig. 2 for low photon energies the first direct interband transition (open circle) occurs from band No. 5 (Λ^3_6) near L for $h\nu \simeq 6.5$ eV. The corresponding spectrum in Fig. 3 for $h\nu = 7.0$ eV clearly exhibits the expected negative sign of the ESP for this transition. The low ESP in that spectrum to some extent may be attributed to the finite $\vec{k}$-space resolution of the present experiment especially for small kinetic energies of the photoelectrons (between $h\nu = 6.5$ and 7.0 eV no differences in the spin polarization have been found within the experimental uncertainties). More satisfactorily it may be explained by the small transition probability near L (in the nonrelativistic limit, at L direct transitions from the d bands to band No. 7 are strictly forbidden) and by a strong admixture of essentially unpolarized electrons from non-$k_\perp$-conserving transitions.[12] The possible origin of these transitions is band No. 5 along the Q line which gives rise to a maximum in the total density of states just below

E_F.[13] For increasing photon energy the probability for the direct transition $5 \rightarrow 7$ must increase since it moves further and further away from the L point.

As a consequence, the negative ESP, produced in that transition, is more clearly seen in Fig. 3 for $h\nu = 8.5$ eV. Emission from the upper occupied Λ^3_{4+5} band (No. 6, filled triangle) sets in near $h\nu = 8.8$ eV with the expected positive ESP. The corresponding ESP curve shows now very clearly the spin-resolved upper Λ^3_{4+5}, Λ^3_6 doublet. If $h\nu$ is increased towards 14 eV, the two components of the lower Λ^3_6, Λ^3_{4+5} doublet (bands No. 3, open square, and No. 2, filled lozenge) emerge with the predicted sign of the ESP. The sequence of spectra from $h\nu = 8.8$ to 17 eV shows that the information from the electron spin does lead to an unequivocal identification of the symmetry character of the initial bands. It further allows for a precise determination of initial-state energies and therefore represents a sensitive test for theoretical band-structure calculations.

For higher photon energies ($h\nu > 20$ eV) the interpretation of the data within the ground-state band structure becomes more and more inadequate since self-energy corrections for the final states may then be important. These corrections tend to lift the hybridization of bands No. 7 and No. 8 at 17 eV and make the dispersion of band No. 7 essentially parabolalike. The higher bands Nos. 8–10 do not give rise to primary-cone photoemission and consequently our data (symbols with crosses) may be interpreted with the assumption of a single free-electron-like final-state parabola.

Though we find good agreement in the sign and the energetic position of the peaks, the measured ESP is less than the $\pm 100\%$ predicted[4] for direct transitions into nonhybridized final states.[14] The experimental resolution clearly plays a role, but even with a better resolution, we found that the ESP also for the leading peak never exceeded $\pm 55\%$. Surface umklapp processes which allow electrons of different polarization from other $\vec{k}$ directions to contribute to normal emission require higher excitation energies $h\nu$ than are actually used in the present study and can therefore be ruled out for $h\nu \leq 20$ eV.

In conclusion, the photoemission from nonmagnetic crystals by circularly polarized light with subsequent electron spin-polarization analysis provides a quantitative experimental characterization of the symmetry properties of electron bands.

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