Experimental Verification of a New Spin-Polarization Effect in Photoemission: Polarized Photoelectrons from Pt(111) with Linearly Polarized Radiation in Normal Incidence and Normal Emission

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A theoretical prediction of a new spin effect by Tamura, Piepke, and Feder has been experimentally verified: Photoelectrons can be polarized even if the photoemission is performed with linearly polarized radiation and even if it is studied in the highly symmetrical setup of normal incidence and normal emission. Radiation with energies between 21 and 22.4 eV ejects photoelectrons from Pt(111) with a degree of polarization between 10% and 40%. The spin direction coincides with a plane parallel to the surface and changes its sign when the crystal is rotated by 60° about the surface normal.

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The existence of spin-polarized photoelectrons obtained with *circularly* polarized radiation from *unpolarized* targets (free atoms, molecules, adsorbates, and nonferromagnetic solids) has been proved to be a common phenomenon rather than exceptional.[1] The spin-polarization information is an important tool to characterize the symmetry of the states and bands involved, i.e., to perform a symmetry-resolved band mapping of solids or a characterization of quantum numbers, dipole matrix elements, or phase-shift differences of wave functions in the photoionization of free or adsorbed atoms.[1,2]

That *linearly* or even unpolarized radiation is able to eject polarized electrons in photoemission of ferromagnetic solids,[3] in which the photoelectron polarization is primarily an effect of the initial states, is well known. In photoionization of free unpolarized atoms and molecules[4] or in photoemission of nonferromagnetic solids[5] it has been found in angle-resolved *off-normal* photoelectron emission as a final-state effect; in these cases it is a consequence of a quantum-mechanical interference between different photoelectron partial waves in atomic photoionization,[6] or due to spin-dependent photoelectron diffraction or phase-matching conditions at the solid-vacuum interface in photoemission.[7] In spin-resolved photoemission from noncentrosymmetric crystals spin polarization can arise from difference in spin-up and spin-down conduction-band hydridization with valence p states and from surface-transmission effects.[8]

Normal incidence of linearly polarized light along centrosymmetric cubic crystals and *normal* photoelectron *emission* was, however, commonly assumed to yield no spin polarization at all.[7,9] Very recently, Tamura, Piepke, and Feder[10] refuted this belief and predicted normal-emission photoelectron spin polarization by linearly polarized light for (111) surfaces of centrosymmetric cubic crystals. Their prediction is based upon a one-step photoemission theory using a relativistic multiple-scattering formalism and they identify the spin-orbit interaction in the half-space initial states as its main cause. In general, symmetry arguments show that for this special geometry electron spin polarization P can be nonzero. Because of the invariance of the total system (semi-infinite crystal with surface, incident light, electron detection direction) under a symmetry operation, photoelectrons can only be polarized perpendicular to a mirror plane. This implies $P=0$ for surfaces with n-fold rotation axes associated with the point groups C_{nv}, $n=2$, 4, and 6, because there are two or more mirror planes perpendicular to one another. For $n=3$ there is not such a restriction. For photoexcitation in the bulk of a centrosymmetric crystal, however, space inversion and time reversal imply $P=0$. A nonzero P appears to be possible therefore in cases in which, for $n=3$, a three-step model is not applicable [like emission from clean surface states or via evanescent states (band-gap emission) from centrosymmetric crystals]. The present Letter is the first experimental evidence that such a spin-polarization effect exists for normal incidence of linearly polarized light and normal photoelectron emission. Along the Λ direction of Pt(111) we find electron spin polarization ranging up to more than 30% for photon energies between 21 and 22.4 eV.

The experiments were performed with linearly polarized synchrotron radiation from the BESSY storage-ring plane and with the 6.5-m normal-incidence monochromator[11] in an apparatus described previously.[12,13] The Pt-crystal surface coincided within 0.5° with the (111) direction and was aligned within 0.3° with the direction of the incident light. Photoelectrons emitted normally to the surface were collected by the electron spectrometer within an angular cone of ±3°. Phonon effects[14] were minimized by our keeping the crystal at a temperature below 50 K during the measurements. The target preparation was performed as usual[12,13] and included Ne^+ bombardment, oxygen heating, and flashing. The surface was characterized by Auger spectroscopy and LEED. LEED was also applied to determine the mirror planes of the Pt(111) crystal. Two spin-polarization components were measured simultaneously in the Mott detector: one parallel to the surface normal (coinciding with the photon momentum), and the other parallel to the crystal surface but at 45° with respect to the storage-ring plane (and thus to the **E** vector of the linearly polarized radiation).[12,13] Influences of experimental asymmetries have been eliminated in the data presented by the use of four additional detectors in forward scattering directions in the Mott detector,[12,13] as well as by the use of count rates in the Mott detector when unpolarized electrons are spin analyzed there.

A photoemission spectrum of Pt(111) obtained with linearly polarized radiation of photon energy $h\nu = 21$ eV is given in Fig. 1(a). Two peaks were obtained: The first at 1.5 eV below E_F (peak 1) corresponds to transitions from the upper initial bands of the bulk band structure close to Γ; the second one at 4 eV below E_F (peak 2) is correlated with a transition from the lower $\Lambda^3_{4,5}$ band (see, e.g., Eyers *et al.*[12]; for the bulk band structure see Fig. 3 of the present Letter). For both peaks a spin analysis of the photoelectrons was made: The combination of photoelectron intensity I and polarization P according to $I_\pm = I(1 \pm P)/2$ yields the partial intensities $I_{+,-}$ characterizing the number of photoelectrons with spin parallel or antiparallel to the Mott-detector analyzing axis. This procedure shows that the spin-polarization component perpendicular to the Pt(111) surface vanishes for both peaks within the experimental uncertainty (3%). The same is true for the component in the Pt(111) surface plane for peak 2 [$I_+ = I_-$ in Fig. 1(a)], whereas peak 1 clearly demonstrates the existence of polarized electrons ($I_+ \neq I_-$) (it corresponds to about 20% spin polarization). All the findings are reproduced by a recent calculation of Tamura and Feder[15] given in Fig. 1(b). The results can be compared despite the fact that they were obtained for photon energies differing by 1 eV, since the calculation neglects a self-energy correction of about the same magnitude (0.75 eV, see Wern *et al.*[16]). While we find good qualitative agreement for the total intensities (a convolution of the calculated spectra with the experimental resolution of 250 meV will mainly broaden peak 1), the polarization values in peak 1 and peak 2 are in excellent agreement with the theoretical results.

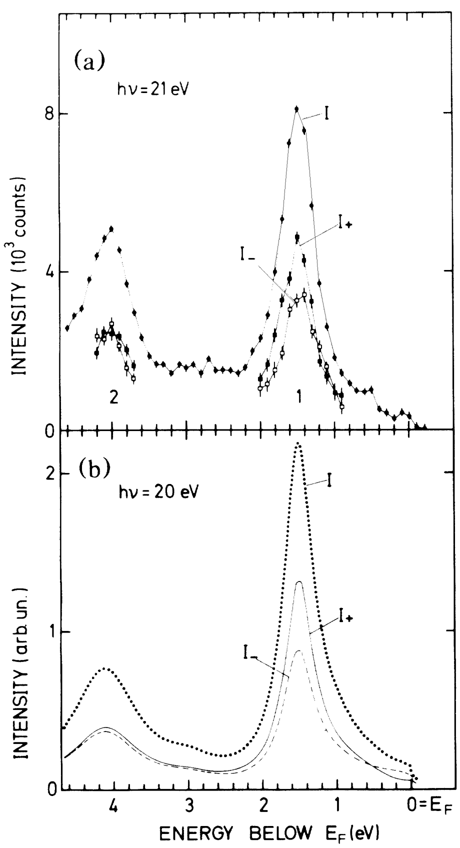

FIG. 1. Photoelectron spectrum obtained from normal incidence of linearly polarized light and normal photoelectron emission. The partial intensities I_+ and I_- correspond to spin directions parallel and antiparallel to a trace of a nonmirror plane in the Pt(111) surface which is rotated by 30° with respect to a trace of a mirror plane in the Pt(111) surface and by 45° with respect to the **E** vector of the incident light. (a) Experimental result (energy resolution $\Delta E = 250$ meV). (b) Calculation of Tamura and Feder (Ref. 15).

Tamura, Piepke, and Feder predicted that the spin-polarization vector is in a plane parallel to the (111) surface and rotates by an angle -2α upon rotation of the light polarization by α (see Fig. 1 of Ref. 10). In our experimental geometry the analyzing axis of our spin Mott detector and the **E** vector of the synchrotron radiation are fixed in space, and so the crystal surface is rotated about the surface normal. For this geometry, the Tamura-Piepke-Feder prediction means that the spin polarization reverses sign when the crystal is rotated by 60°.

For further elucidation of the effect, the dependence of the spin polarization on the rotation angle ω of the crystal about the surface normal has been measured. The upper part of Fig. 2 shows the angular dependence of the ratios of count rates N_B/N_D and N_A/N_C directly measured by the detectors of the Mott detector. N_B/N_D corresponds to the out-of-plane [Pt(111) plane] polarization, and N_A/N_C to the in-plane polarization. The corresponding detector setup is given in the schematic diagram. While there is no angular dependence of N_B/N_D within the experimental uncertainty, N_A/N_C demonstrates a clear sinusoidal shape as a function of the angle ω. Instrument-related asymmetries (due to different detector efficiencies, scattering solid angles, etc.) are responsible for the fact that the ω-averaged asymmetry is different from 1, but they are independent of ω. From the measured asymmetry data one obtains the spin-polarization component P_{xy} in the crystal plane. These values are presented in the lower part of Fig. 2. For

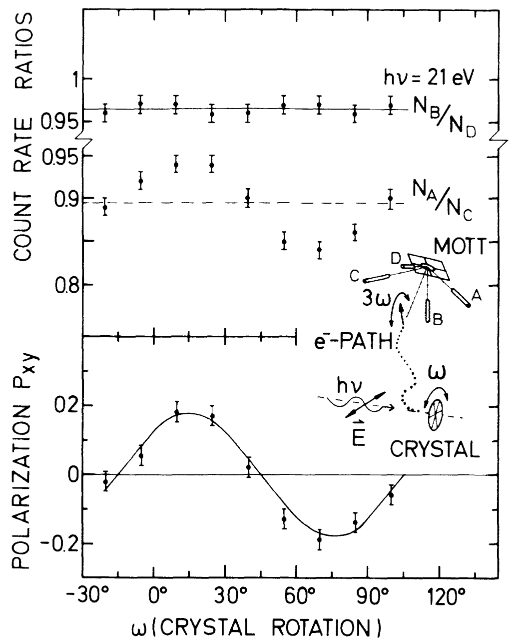

FIG. 2. Photoelectron spin polarization P_{xy} in the first peak of the photoelectron spectrum (Fig. 1) obtained for normal incidence of linearly polarized light and normal photoelectron emission. Top: Ratios of the Mott-detector count rates N_A/N_C and N_B/N_D vs the rotation angle ω about the Pt(111) surface normal. Inset: Relation of spin-polarization directions and Mott-counter arrangement. The spin-polarization vector rotates in a plane parallel to the surface and thus parallel to the plane spanned by the Mott counters B and D. Bottom: Dependence of P_{xy} on the crystal rotation angle ω.

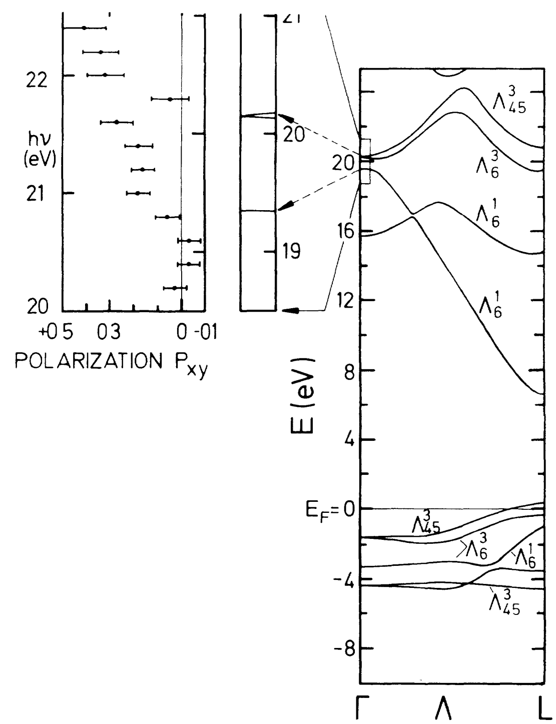

FIG. 3. Comparison of experimental photoelectron spin-polarization values P_{xy} with a bulk band-structure calculation. The polarization values P_{xy} were obtained for normal incidence of linearly polarized light and normal photoelectron emission and correspond to transitions from the upper initial bands near Γ (1.5 eV below E_F) to the final part of the band structure. Left-hand side: Dependence of P_{xy} on the photon energy $h\nu$ for the initial energy -1.5 eV. Right-hand side: Bulk band structure (Ref. 15). Middle: Final bands at about 20 eV at Γ in an expanded energy scale. High polarization values occur for transitions into band gaps.

$\omega = 0°$ the crystal mirror plane and the storage-ring plane are parallel. The data show a periodicity of 120° and can be well described by a sinusoidal behavior (continuous line in Fig. 2). We find maximum polarization for $\omega \simeq 15°$, i.e., a spin rotation of $3\omega \simeq 45°$, which agrees with our experimental setup of the analyzing axis of the Mott detector (45° with respect to **E**) as discussed above.

In addition to these results the measurements were extended to photon energies $h\nu$ between 20 and 22.4 eV. Figure 3 (left-hand side) shows the spin polarization P_{xy} of a constant-initial-state spectrum obtained for the initial energy 1.5 eV below E_F. Below $h\nu = 20.8$ eV we do not find a spin polarization within the experimental accuracy, while the polarization seems to increase gradually with increasing photon energy except for a breakdown at 21.8 eV. For a rough interpretation of the results we compare the energy dependence of the spin polarization with a bulk band structure of Tamura and Feder, which is shifted by the self-energy correction value of 0.75 eV (Ref. 16) towards higher energies. From the comparison we find that the polarization onset at 20.8 eV is correlated with an onset of transitions into the narrow band gap between 19.3- and 20.2-eV final energy. The breakdown of the polarization occurs at that point of the band structure where the Λ_3 bands meet the Γ point. All these findings are in agreement with the interpretation that transitions into the band gap produce the spin polarization. The threefold symmetry of Pt(111) and the surface are thus observed, because the electron emission occurs via Λ_6^1 evanescent states.[17]

Summarizing, we have reported experimental evidence of a new spin-polarization effect. Spin-polarized photoelectrons are obtained with linearly polarized light in the highly symmetrical experimental setup of normal light incidence and normal photoelectron emission from Pt(111). The spin-polarization direction is parallel to the surface. We observe polarization up to more than 30%, a sinusoidal behavior with the rotation angle ω about the Pt(111) surface, and a 120° periodicity according to the threefold symmetry of Pt(111) and the inclusion of the surface. The observed surface effect is obviously of the same nature as that predicted by Tamura, Piepke, and Feder.[10]

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