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Experimental verification of a spin effect in photoemission: Polarized electrons due to phase-shift differences in the normal emission from Pt(100) by unpolarized radiation

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A theoretical prediction of Tamura and Feder has been experimentally verified: Photoelectrons from the fourfold-symmetric surface of a centrosymmetric crystal, Pt(100), can be polarized even if the incident radiation is unpolarized and the electrons are emitted normal to the surface. For 21.2- and 16.9-eV photon energies, a spin-polarization component P_y perpendicular to the reaction plane is found. The degree of polarization is up to 15% and does not change when the crystal is rotated about its surface normal. This supports strongly the prediction that the effect is due to phase-shift differences.

This work reports on the experimental verification of an effect in photoemission that produces spin-polarized electrons without making use of magnetically ordered electron spins (as in photoemission from magnetic materials[1]) or of optical spin orientation by excitation with circularly polarized light.[2] It was predicted in a recent theoretical work by Tamura and Feder[3] and yields spin-polarized electrons with unpolarized light even in the normal photoemission from the fourfold-symmetrical Pt(100) surface, for which other earlier reported spin-polarization effects with linearly and unpolarized radiation from nonmagnetic crystals are forbidden by symmetry (see below). The effect has its origin in a broken symmetry due to off-normal light incidence in combination with hybridization [$\Delta_6^1\Delta_6^5$ hybrids for (100) surfaces] and yields spin-polarized electrons due to phase-shift differences. The spin-polarization vector **P** is perpendicular to the reaction plane of the incident radiation and the emitted electrons. The effect is only predicted for the "one-step model" of photoemission, while it is absent in the "three-step model."[3] It is expected[3] to occur for practically each crystal surface, which makes it widely applicable. In photoemission from ferromagnetic samples, for example, it competes with exchange-induced effects and might influence the interpretation of spin-resolved photoemission spectra and conclusions concerning ferromagnetic properties.[4]

There have been previous reports in the angle-resolved photoemission from nonmagnetic materials with linearly and unpolarized radiation but they all differ fundamentally from the effect reported in this work: In Ref. 5 spin-polarized electrons arise from spin-dependent photoelectron diffraction or phase matching conditions at the solid vacuum interface and are only obtained when the electron emission occurs *off normal.* Spin-polarized electron emission with linearly and unpolarized light was also observed in the photoionization of free unpolarized atoms and molecules[6] where it is a consequence of a quantum-mechanical interference between different photoelectron partial waves. It was, however, until now not clear whether a counterpart of this effect for *solids* can exist at all.[3] Even for *normal* photoemission with linearly and unpolarized light from nonmagnetic crystals spin-polarized electrons were found when the sample is *noncentrosymmetric.*[7] Phase shifts do not, however, play any role in this case and in contrast to the present one this effect does not occur for photoelectron emission along the [100] and [111] lines. Spin-polarized electrons have been predicted[8] and experimentally verified[9] for the normal photoemission from a nonmagnetic and centrosymmetric surface, namely, the special case of *normal* incidence of *linearly* polarized radiation from *threefold-symmetric surfaces.* This effect does not exist for the two-, four-, and sixfold-symmetric surfaces. Recently it was also shown to be suitable for a study of adsorbate systems.[10] Hybridization is not needed for this effect and spin-polarized electrons can only be obtained when bands with symmetry $\Lambda_{4,5}^3$ are involved in the transitions.

The different physical mechanisms which are responsible for the three spin-polarization effects described in Refs. 7, 8–10, and 3 are also reflected in the dependence of the spin-polarization vector **P** on a rotation ϕ of the crystal about the surface normal: In all cases **P** is parallel to the crystal surface but in Ref. 7 **P** remains fixed with respect to the crystal, in Refs. 8–10 **P** rotates by an angle 3ϕ, and in Ref. 3 **P** remains fixed in the laboratory system, i.e., its direction is only determined by the direction of the incident photon and the emitted electron but not by crystal properties.

The experimental setup is given in Fig. 1. Unpolarized radiation hits the Pt(100) surface at an angle of 62° with respect to the surface normal. The normally emitted electrons are energy analyzed electrostatically. Two components of the spin-polarization vector are determined by Mott scattering.[11] One is perpendicular to the reaction plane (P_y), the second one (P_z) parallel to the surface normal of Pt(100). P_z turned out to be zero for all measurements. The crystal preparation is done by sputtering and heating in oxygen and the surface was characterized by low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES). The preparation result was a clean reconstructed 5×1 surface; a 1×1 surface was obtained by CO adsorption (as in Ref. 12).

For the 1×1 surface and He I radiation incidence at an angle of 62° we obtain the photoemission spectrum in the upper part of Fig. 2 with two broad peaks. The total in-

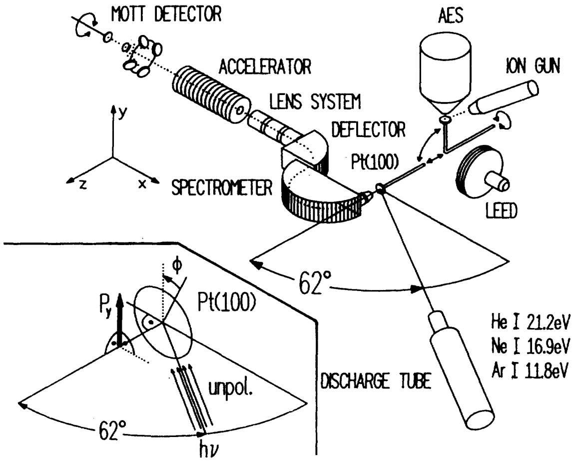

FIG. 1. Experimental setup.

tensity I (dots with solid line) is separated into the partial intensities for spin up (+) and down (−) $I_\pm=(I/2)(1\pm P_y)$ by means of the spin-polarization component P_y perpendicular to the reaction plane. The electrons from both peaks in the photoemission spectrum are strongly spin polarized, the first one below E_F turns out to be a peak in I_-, the second one a peak in I_+. In Ref. 3 it was predicted that P_y should show no change during a rotation ϕ of the crystal about the surface normal. For a binding energy of 2.2 eV (indicated by an arrow in the upper part of Fig. 2) the dependence of P_y on ϕ has been measured and is displayed in the lower part of Fig. 2. Within the experimental error there is indeed no change of P_y with ϕ.

A corresponding spectrum was also measured for the reconstructed Pt(100) 5×1 surface (upper left part of Fig. 3). Comparing it with the corresponding spectrum for the 1×1 surface in Fig. 2 we note mainly a change in peak shape of the peak between 0- and 3-eV binding energy which is due to surface states for the reconstructed surface.[12] The spin polarization is, however, not strongly affected by these transitions. Studies have also been performed at the other photon energies of 16.9 eV (Ne I) and 11.8 eV (Ar I) in order to find out whether the occurrence of spin-polarized electrons is a special effect for a certain electronic transition at a certain photon energy (21.2 eV) or a more general phenomenon. For 16.9-eV photon energy the photoemission spectrum is displayed in the middle left part of Fig. 3. For the main peak between E_F and 3 eV below E_F we find again (as for 21.2 eV) strongly negatively spin-polarized electrons. The lower left part of

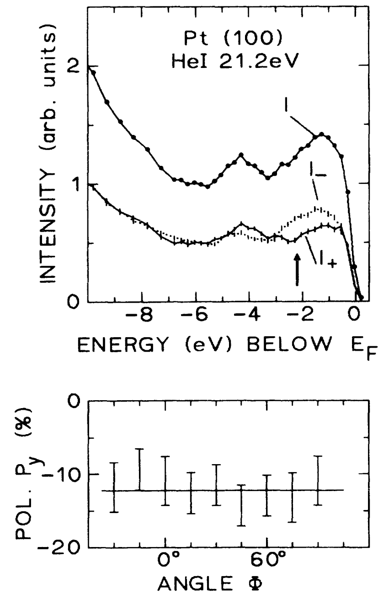

FIG. 2. Top: Photoemission spectrum obtained with unpolarized He I radiation for normal emission from a 1×1 surface of Pt(100). I denotes the total intensity, I_+ and I_- are the partial intensities with spin up and down, respectively. Vertical dashes in the I_+ and I_- intensities represent the total experimental error including the statistical error of the count rates and the uncertainty of the detector asymmetry function. The arrow at −2.2 eV indicates the energetic position for which the dependence of P_y on ϕ was determined. Bottom: Dependence of the spin-polarization component P_y on the rotation ϕ of the Pt(100) crystal about the surface normal. No variation is observed within the experimental accuracy.

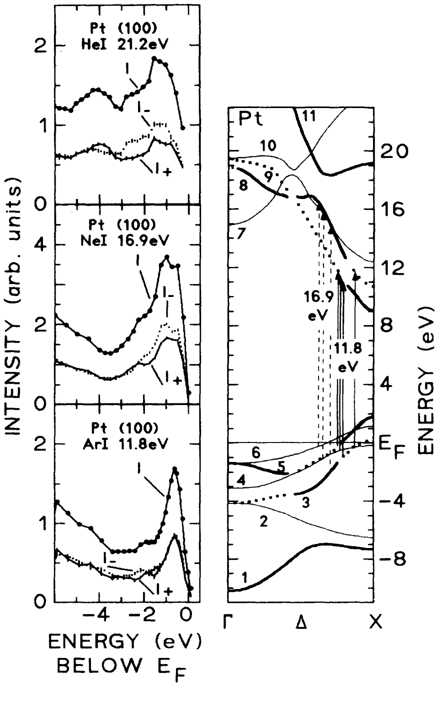

FIG. 3. Left part: Spin-polarized photoemission spectra obtained with unpolarized radiation for normal emission from a 5×1 surface of Pt(100) and three different photon energies. The meaning of the symbols is identical to that in the upper part of Fig. 2. Right part: Band structure of Pt in the Δ direction. The band structure has been calculated by Noffke and Eckardt (Ref. 13). Heavy solid lines (–) denote bands with Δ_6^1 symmetry, dots (· ·) those with Δ_6^5 symmetry. Thin solid lines are bands with Δ_7 symmetry. Arrows indicate the transitions which contribute to two of the three spectra in the left column of Fig. 3.

Fig. 3 shows the spectrum for 11.8 eV; the main peak in the photoemission spectrum is considerably narrowed compared to that at higher photon energies and the electrons contributing to this peak are not spin polarized.

In order to reveal possible reasons for the dependence of the spin-polarization structure on photon energy we discuss the data together with a band structure. Of course we have in mind the prediction of Tamura and Feder that the mechanism that produces the spin polarization needs spin-orbit-induced hybridization of Δ_6^1 and Δ_6^5 bands.

The band structure shown in Fig. 3 is a calculation of Noffke and Eckardt.[13] Bands with Δ_6^1 symmetry (i.e., bands with dominating Δ_1 spatial part) are represented by the heavy lines, bands with Δ_6^5 symmetry (i.e., dominating Δ_5 spatial part) by dots. Thin solid lines are bands with symmetry Δ_7 which should only contribute to the spin polarization,[3] if the transitions occur into a $\Delta_6^1\Delta_6^5$ hybrid. The main bands under consideration, 3, 5, 8, and 9, are hybridized for almost all $k_\perp$ values along Δ. The degree of hybridization is a maximum close to avoided crossing points. It seems strange that the spin polarization vanishes for 11.8 eV, where transitions occur between areas of strongest hybridization close to the avoided crossing points, while a considerable degree of spin polarization is observed for $h\nu = 16.9$ eV where the transitions occur between bands with a lower degree of hybridization. Thus we do not see a simple correlation of the spin polarization with the degree of band hybridization in this first work.

In order to gain a further understanding for the mechanism that produces the spin-polarization effect we discuss some striking similarities of this spin-polarization effect with a well-known spin-polarization effect in photoionization.[6] Tamura and Feder predicted[3] that

$$P_y \propto \sin(2\theta)\,\mathrm{Im}(m_\parallel m_\perp^*) \tag{1}$$

with $m_\parallel$ and $m_\perp$ being the transition matrix elements for excitation with the components of the $\mathbf{E}$ vector of the incident radiation parallel and perpendicular to the crystal surface and θ the incidence angle of the radiation with respect to the surface normal. Spin-polarized electrons can also be obtained by photoionization of free atoms and molecules with unpolarized radiation, if the electron emission occurs at a nonzero angle θ with respect to the direction of the incident radiation.[6,14] $\mathbf{P}$ is then also perpendicular to the reaction plane and

$$|\mathbf{P}| \propto \sin(2\theta)\,\mathrm{Im}(D_1 D_2^*)\ . \tag{2}$$

D_1 and D_2 denote the complex transition matrix elements for transitions from one initial state into two different but energetically degenerated continuum states.[6,14] Spin polarization is due to a quantum-mechanical interference of these continuum waves and yields only a nonzero value of $\mathrm{Im}(D_1 D_2^*)$ if a phase-shift difference exists between the two waves.[14] Furthermore the photoionization spin polarizations from spin-orbit-split initial states have opposite signs, showing the responsibility of the spin-orbit interaction for the photoelectron polarization and the necessity to resolve its influence by means of an electron spectrometer for photoelectron spectroscopy. It seems to be obvious from relation (1) that the physical mechanism that produces the spin polarization P_y is closely related to that in photoionization firstly because of the same formula description, secondly because of the fact that phase-shift differences of energy degenerated final states due to complex matrix elements can only exist in the one-step photoemission treatment, and thirdly because of the necessity of spin-orbit-induced hybridization in the ground state.

If phase differences determine the size and sign of the spin polarization it is at once clear why an easy relation between the spin polarization and degree of hybridization as discussed in Fig. 3 cannot be expected. In turn the data contain then, however, information about these phase-shift differences. On the way to a "complete" experiment,[11] i.e., the complete characterization of the photoelectron emission process by experimental determination of all individual matrix elements and phase-shift differences, as it has been done in atomic and molecular photoionization,[14] the data presented in the letter complement information of other photoemission types: off-normal spin-resolved photoelectron emission using circularly polarized radiation[15] and circular dichroism in the angular distribution of photoelectron intensities.[16] Whether this puzzle of different techniques to a "complete" characterization also works for solid surfaces as for free atoms and adsorbates is a question which requires a further experimental and theoretical study and is beyond the scope of this paper.

In conclusion this work has reported on the experimental verification of a spin-polarization effect for photoemission with off-normal incident *unpolarized* radiation from the highly symmetrical fourfold-symmetric (100) surface of Pt and *normal* electron emission. The experimental findings agree with a recent theoretical prediction of Tamura and Feder[3] who pointed out that the effect requires spin-orbit-induced $\Delta_6^1\Delta_6^5$ hybridization. Striking similarities exist also with a similar effect in photoionization of free atoms and molecules[6,14] where the spin polarization arises from phase-shift differences of final-state wave functions. In view of the high spin-polarization values measured it seems worth mentioning that this spin-orbit-induced effect is theoretically expected for any surface symmetry and might thus also occur in photoemission of other nonmagnetic and ferromagnetic samples because of the general importance of hybridization in electronic band structures.

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