New Spin-Polarization Effect in Photoemission from Nonmagnetic Surfaces

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Symmetry arguments and analytical calculation show that—contrary to common belief—photoelectrons emitted normal to (111) surfaces of nonmagnetic centrosymmetric cubic crystals by normally incident linearly polarized light may be spin polarized. Their spin is parallel to the surface and rotates by an angle 2α upon rotation of the light polarization by α. Numerical calculations using a relativistic multiple-scattering formalism explicitly predict the effect for Pt(111), with a polarization up to 70%, and identify spin-orbit coupling in half-space initial states as its main cause.

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A growing number of recent experimental and theoretical studies have clearly demonstrated that analysis of the electron-spin polarization in momentum-resolved photoemission spectroscopy provides valuable information both on the electronic structure of the system under study and on the emission mechanism, which cannot be obtained from intensity spectra (for reviews and references, cf. Refs. 1–4). While obvious in the case of a ferromagnetically ordered ground state (for ferromagnetic clean surfaces, epitaxial and adsorbate systems), this is also true for nonmagnetic systems (atoms, molecules, solid surfaces) as a consequence of spin-orbit coupling. In the latter category, attention has mainly focused on photoelectron-spin polarization produced by circularly polarized radiation, in particular for photon incidence and electron emission along high-symmetry lines (especially directions normal to low-index crystal surfaces). For such geometry and centrosymmetric crystals, linearly polarized light, however, has commonly been believed to produce no spin polarization at all (Refs. 1 and 2, Wöhlecke and Borstel,[5] Borstel,[6] and Ginatempo *et al.*,[7] and references therein). The present Letter refutes this belief. For (111) surfaces of centrosymmetric cubic crystals, we predict normal-emission photoelectron-spin polarization by linearly polarized light, using a three-pronged approach: (a) general symmetry arguments, (b) analytical evaluation of dipole transition matrix elements, and (c) realistic numerical calculations based on a relativistic "one-step" photoemission theory. Fundamental and practical implications of this new type of spin-polarization effect will be discussed.

In passing to general symmetry considerations, we recall (cf., e.g., Ref. 1) that the spin polarization vector $\mathbf{P}(E)$ and intensity $I(E)$ of the photocurrent at normal emission (i.e., with surface-parallel momentum $\mathbf{k}_\parallel=0$) are obtained from its spin-density matrix $\rho(E)$ as $I(E)=\mathrm{tr}[\rho(e)]$ and $\mathbf{P}(E)=\mathrm{tr}[\boldsymbol{\sigma}\rho(E)]/I(E)$, where $\boldsymbol{\sigma}=\hbar(\sigma_x,\sigma_y,\sigma_z)/2$ is the Pauli spin operator. Invariance of the total system (semi-infinite crystal with surface, incident light, electron detection direction) under a symmetry operation implies invariance of $\rho(E)$ and consequently restrictions on $\mathbf{P}(E)$. For example, an (x,z) mirror plane (with z along the surface normal, and $M_1=-i\sigma_y$ representing the mirror operation in spin space) implies $\rho=M_1^\dagger\rho M_1$ and thence $P_x=P_z=0$, i.e., photoelectrons can be polarized only perpendicular to the mirror plane. Similarly, a (y,z) mirror plane, with operation M_2, dictates $P_y=P_z=0$. Thus, the existence of two mirror planes (of the crystal) normal to the surface and to each other leads to $\mathbf{P}=0$ at normal emission and for radiation linearly polarized with $\mathbf{E}\parallel\hat{\mathbf{x}}$ or $\hat{\mathbf{y}}$. (For $\mathbf{E}$ in an arbitrary direction parallel to the surface, the combined operation M_2M_1 leads to $\mathbf{P}=0$.) Therefore, $\mathbf{P}=0$ for surfaces with n-fold rotation axes associated with the point groups C_{nv}, for $n=2,4,6$. For $n=3$, however, there is no mirror plane perpendicular to the $(1\bar{1}0)$ mirror plane (nor to the other two obtained by $2\pi/3$ rotations). Consequently, for $\mathbf{E}\parallel\hat{\mathbf{x}}$ or $\hat{\mathbf{y}}$, $P_y\neq0$ appears possible. For unpolarized light, which can be regarded as an incoherent superposition of two oppositely circularly polarized contributions, the total setup exhibits a further symmetry: rotations about the z axis by $\alpha=2\pi/3$ and $4\pi/3$. Invariance of the photocurrent spin-density matrix ρ yields $P_x^{\mathrm{un}}=0=P_y^{\mathrm{un}}$, i.e., no spin polarization in the plane. ($P_z^{\mathrm{un}}=0$ follows from the mirror operation.) Since unpolarized light can equivalently be regarded as a superposition of linearly polarized light with $\mathbf{E}(\alpha)$ and $\mathbf{E}(\alpha+\pi/2)$, where α is the azimuthal angle in the (x,y) plane (with $\alpha=0$ along the $+x$ axis), this implies that for linearly polarized light $P_y(\alpha=0)=-P_y(\alpha=\pi/2)$, and, more generally, $\mathbf{P}_\parallel(\alpha)=-\mathbf{P}_\parallel(\alpha+\pi/2)$, where $\mathbf{P}_\parallel=(P_x,P_y)$. From mirror symmetry we find $P_x(-\alpha)=-P_x(\alpha)$ and $P_y(-\alpha)=P_y(\alpha)$. Since $\alpha+\pi$ is physically equivalent to α, we further have $\mathbf{P}_\parallel(\alpha+\pi)=\mathbf{P}_\parallel(\alpha)$. In summary, we find for linearly polarized light the electron-spin polarization (illustrated in Fig. 1)

$$P_x(\alpha)=\sin2\alpha P_y(0),\quad P_y(\alpha)=\cos2\alpha P_y(0). \qquad (1)$$

A rotation of the light polarization relative to the (x,z) mirror plane by an angle α thus leads to a rotation by -2α of the spin-polarization vector. If the latter is significantly nonzero, Eq. (1) promises a sensitive check

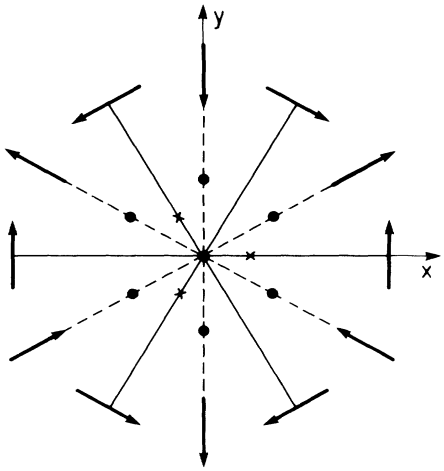

FIG. 1. Photoemission normal to cubic-lattice (111) surfaces (paper plane). For linearly polarized light with **E** parallel to the thin lines (full and dashed line indicating traces of surface-normal mirror and nonmirror planes, respectively), the directions of the photoelectron-spin-polarization vector are given by the thick arrows at the ends of lines [cf. Eq. (1)].

on experimental accuracy in spin-resolved photoemission spectroscopy.

The crucial question is now whether $\mathbf{P}_\parallel$ is actually generally nonvanishing. In the framework of the "three-step model" of photoemission, in which the entire process is regarded as a succession of (a) bulk (infinite solid) excitation, (b) transport to the surface, and (c) transmission into the vacuum (cf. Ref. 1 and references therein), one obtains, in fact, $\mathbf{P}=0$ for centrosymmetric crystals. In step (a), invariance of the entire "setup" under space inversion J and time reversal T implies $\mathbf{P}_b=\mathrm{tr}[\boldsymbol{\sigma}\rho] =\mathrm{tr}[\boldsymbol{\sigma}(JT)^\dagger\rho(JT)] = -\mathbf{P}_b$ and hence $\mathbf{P}_b=0$ (Ref. 1, p. 215). The same result is obtained by evaluation of dipole matrix elements by use of JT transforms of initial and final states.[5] Since transmission perpendicular to the surface and transport are spin independent, the photocurrent is unpolarized. It is important to note that the above JT based argument does not hold for the more realistic "one-step model," in which initial and final states belong to a semi-infinite (half-space) crystal Hamiltonian. The latter obviously is not invariant under space inversion J. A nonzero $\mathbf{P}_\parallel$ appears therefore possible in cases in which a three-step model is not applicable (like emission from clean-surface states and adsorbate levels).

Whether $\mathbf{P}_\parallel\neq 0$ at (111) surfaces does actually occur can be investigated by analytical calculation of the spin-density matrix ρ. Since this is rather lengthy and technical, we shall present the details elsewhere[8] and focus here only on some salient features and on the results. We started along established lines (cf., e.g., Refs. 1 and 5), which requires the calculation of dipole matrix elements $\langle f|H'|i\rangle$, with $H'=\mathbf{E}\cdot\mathbf{r}$ and, especially for linearly polarized light (at angle α relative to x axis), $\mathbf{E}=E_0(\cos\alpha,\sin\alpha)$. The final states $|f\rangle$, which are of the form $e^{-ikz}\chi^\sigma$ outside the crystal (χ^+ and χ^- being two Pauli spinors), belong to the two-dimensional extra irreducible representation Λ_6 of the double group C_{3v}. Relativistic dipole selection rules (cf. Refs. 1 and 5) permit initial states $|i\rangle$ of symmetries Λ_6 and Λ_{4+5}, with the latter consisting of two one-dimensional irreducible representations Λ_4 and Λ_5, which are coupled by the time reversal operation T. If $|i_1\rangle=|E,\mathbf{k}_\parallel=0,\sigma\rangle$ is an initital state (half-space solution of the Dirac equation), so is $T|i_1\rangle=|E,\mathbf{k}_\parallel=0,-\sigma\rangle$. Initial and final states are then expressed as general linear combinations of basis functions of the appropriate irreducible representations. Here we notice an important difference between initial states of Λ_6 and of Λ_{4+5} symmetry. Since the former are associated with a 2D irreducible representation, they have only half as many independent combination coefficients as the initial states built from the basis functions of the two 1D representations Λ_4 and Λ_5. This difference strongly affects our results for the off-diagonal elements of the spin-density matrix, which determine P_x and P_y. For Λ_6 symmetry, they are identically zero, while for Λ_{4+5} they contain general expressions, which cannot vanish altogether. For the dependence on the light polarization angle α, we explicitly obtain the relation Eq. (1), which we inferred earlier from general symmetry requirements. Our calculation further shows that $\mathbf{P}_\parallel$ vanishes if either $|i\rangle$ or $|f\rangle$ contains only one basis function rather than a linear combination.

To obtain quantitative predictions for the new polarization effect and its relation to intensity spectra, we employed a relativistic one-step-model photoemission formalism,[1,9] in which initial and final half-space solutions of the Dirac equation are calculated by a multiple-scattering method (layer Korringa-Kohn-Rostoker) and dipole transition matrix elements are evaluated numerically. This formalism was previously found, for circularly polarized radiation, to produce spin-polarization and intensity results[10] in good agreement with experiment[11] for Pt(111). This surface is a most suitable system for pioneering spin-polarization studies, since first, its large nuclear charge ($Z=78$) entails strong spin-orbit coupling, and second, its "truncated-bulk" geometry rules out complications and uncertainties, which occur for "reconstructed" surfaces. We therefore also chose Pt(111) for our present calculations.

Typical results are shown in Fig. 2. The bulk band structure, which we obtained simultaneously (by diagonalizing the layer matrices, cf., e.g., Ref. 1), is included [Fig. 2(c)] since it contributes to the understanding and interpretation of the photoemission results: Crossing points between initial-state bands (solid lines) and the fully symmetric Λ_6 final-state band (displaced downward by the photon energy) indicate energies at which dipole transitions may occur between the relevant Bloch states of the infinite crystal (bulk). In the spirit of

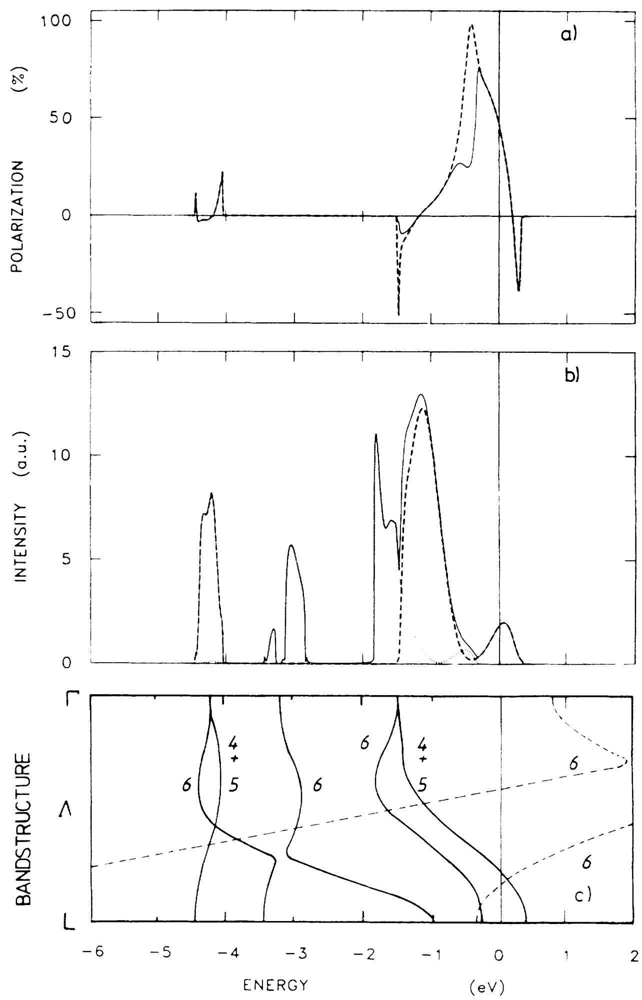

FIG. 2. Photoemission normal to Pt(111) surface induced by normally incident linearly polarized ultraviolet light (with photon energy $\hbar\omega = 14$ eV). (a) Spin polarization parallel to the surface [cf. Eq. (1) and Fig. 1] as a function of the initial-state energy (with 0 corresponding to the Fermi energy E_F for the total (energy resolved) current (solid lines) and its contribution from Λ_{4+5}-symmetry initial states (dashed lines). (b) Total intensity (solid lines) and its contributions from Λ_{4+5} (dashed lines) and Λ_6 (dotted lines) initial states. (c) Relativistic bulk band structure along $\Gamma(\Lambda)L$ for initial states (solid lines) with symmetry as indicated and for Λ_6 final states (shifted downwards in energy by the photon energy) (dashed lines).

a three-step model these lead to maxima in the photocurrent. Our intensity results [Fig. 2(b)] indeed exhibit such peaks, broadened by the lifetime of the final state, which we took into account via an imaginary-potential contribution of 0.5 eV. [Initial-state lifetime effects, which vanish at the Fermi energy E_F and produce a Lorentzian broadening increasing with binding energy (cf., e.g., Ref. 1 and references therein), are not included in the spectra in Fig. 2]. The band crossing near -3.8 eV does not manifest itself, because the Λ_6 initial state at this energy is almost purely of type Λ_6^1 (i.e., has spatial character of the nonrelativistic single-group representation Λ^1) and a Λ_6^3 part is required for the transition matrix elements to the Λ_6^1 final state to be nonzero (for light with polarization vector **E** parallel to the surface) (cf., e.g., Refs. 1 and 5). In addition to these "bulk peaks," we find intensity features—at -4.3, -3.4, -1.8, and -0.5 eV—which are associated with the breakdown of momentum conservation normal to the surface and with a high density of initial states.

The spin polarization $P_y(\alpha=0)$ [cf. Eq. (1)] of the emitted electrons is seen [Fig. 2(a)]—exclusively in energy regions with Λ_{4+5} symmetry initial states, as it should from our above analytical results—to be large and strongly structured. At energies of maximal Λ_{4+5} intensity it goes through zero. This is in line with the above-mentioned absence of the effect for an infinite crystal. Conversely, the polarization of the Λ_{4+5} contribution to the current is maximal (up to 95%) near energies where I is minimal. For the feature around E_F, the slight shift in energy of the polarization zero with respect to the intensity maximum is due to a polarized contribution from an "indirect" (k_z nonconserving) transition to the other Λ_6 final-state band. Taking into account the Fermi cutoff in photoemission (i.e., initial states must be occupied), there is still a large polarization value (about 50%) together with substantial intensity. Convolution by a state-of-the-art experimental energy resolution of 0.1 eV modifies this into about 60% polarization associated with a still distinct intensity peak. The unoccupied part (above E_F) could be observed by inverse photoemission (bremsstrahlung) using polarized electrons (cf., e.g., Ref. 1 and references therein). We note that our findings around E_F are practically unaltered by initial-state lifetime effects (self-energy corrections), since these vanish at E_F. Adding the unpolarized Λ_6 emission current to the polarized Λ_{4+5} current, as experiment does, generally reduces the spin polarization, but still leaves large values [cf. full curve in Fig. 2(a)].

The physical origin of the present spin-polarization effect is further elucidated by our switching off spin-orbit coupling in the calculation of the final or initial state or both. In the last case we obtained of course $P_y=0$, whereas in the first P_y deviates only mildly from the fully relativistic result. For nonrelativistic initial states (of symmetry Λ^3) we found comparatively rather small P_y values (up to about 10%). Spin-orbit coupling in the initial state is thus seen to play the dominant role. This, as well as the zero polarization for unpolarized light in a three-step model of photoemission, fundamentally distinguishes our spin-polarization findings from two established "final-state effects," in which photoelectrons generated by linearly polarized or unpolarized light become polarized by (a) spin-dependent transmission through the surface at off-normal emission[12,13] and (b) spin splitting of bulk final-state bands for noncentrosymmetric crystals.[14] Since the surface is vital for the present polarization phenomenon, one can expect it to respond sensitively to changes in the surface region. Numerical results, which we obtained for different positions of the surface potential barrier (the transitions from the bulk inner potential to the vacuum zero), support this expectation.

In conclusion, we predict that photoelectrons generated normal to cubic (111) surfaces by linearly polarized light can be highly polarized as a consequence of spin-orbit coupling in genuine half-space initial states. The key role of the surface in producing this new spin-polarization effect recommends it as a potential tool for the investigation of geometrical reconstructions of clean surfaces and details of adsorbate systems like the recently intensely studied noble-gas layers on Pt(111).[3,4]

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