Theory of Spin-Polarized Photoemission from Nonmagnetic Metals: Platinum

B. Ginatempo
H. H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom

and

P. J. Durham
Science and Engineering Research Council, Daresbury Laboratory, Warrington, United Kingdom

and

B. L. Gyorffy
H. H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom

and

W. M. Temmerman
Science and Engineering Research Council, Daresbury Laboratory, Warrington, United Kingdom
(Received 1 Feburary 1985)

We develop a fully relativistic theory of the process of photoemission from paramagnetic metals and illustrate it by explicit calculations of the photocurrent and the spin polarization of electrons photoemitted from a single-crystal platinum sample. Our results are in good agreement with the available experimental data and indicate that energy-, angle-, and spin-resolved photoemission spectroscopy is a powerful new probe of the electronic structure even in the case of nonmagnetic metals.

PACS numbers: 79.60.Cn, 75.25.+z

Recently, it has become possible to measure the spin polarization of emitted electrons in an energy- and angle-resolved photoemission experiment.[1] This is a significant advance for it opens up the possibility of studying spin-related features of the electronic structure in crystalline solids as function of energy and wave vector. Indeed, such experiments have already made important contributions to the understanding of metallic magnetism.[2] Moreover, the pioneering work of Eyers *et al.*[3] on Pt suggests that this technique can provide interesting new information even in the case of nonmagnetic metals.

That circularly polarized light can induce photoemission of polarized electrons from an unpolarized target, on account of the spin-orbit interaction, has been known for a long time.[4] However, the measurements of Eyers *et al.*[3] is the first energy- and angle-resolved study of the effect with a crystalline solid as the emitter. In this Letter we present a fully relativistic theory of the photoemission process from a nonmagnetic metal and provide a quantitative interpretation of their experiments.

We describe the photoemission as a one-step transition from the states of a semi-infinite solid to the time-reversed states of low-energy electron diffraction (LEED). In short our theory is a fully relativistic generalization of the nonrelativistic theory of Pendry.[5]

We work in the one-electron picture and use atomic units: $e=\hbar=m=1$, $c=137.036$. The crystal potential is taken to be of the usual "muffin-tin" form with a step of height V_0 at the surface. Such a description of the surface is adequate for uv photons whose wavelengths, λ, are large compared with the physical width of the surface. We also assume that λ is much larger than the Compton wavelength $\hbar/mc$ and the lattice spacing. Consequently we shall make the dipole approximation.

Generalizing the approach of Pendry[5] we generate the time-reversed LEED final state $|\psi_f^{\nu}\rangle$ from the wave function at the detector $\langle \mathbf{r}|f,\nu\rangle$. For this we take the Dirac spinor:

$$\langle r|f,\nu\rangle=\left\{\frac{\epsilon+\omega-V_0+C^2+C^2}{2(\epsilon+\omega-V_0+C^2)}\right\}^{1/2}\begin{pmatrix}\chi_\nu\\ \dfrac{c\,\boldsymbol{\sigma}\cdot\mathbf{k}}{\epsilon+\omega-V_0+C^2}\end{pmatrix}\exp(i\mathbf{k}_{\parallel}\cdot\mathbf{r})\delta(z-z_0), \tag{1}$$

where ω is the frequency of the incident photon, ϵ is the initial energy of the photo-ejected electron, $\epsilon+\omega-V_0$ is its kinetic energy and $\mathbf{k}$ is its wave vector outside the sample, $\mathbf{k}_{\parallel}$ is the component of $\mathbf{k}$ parallel to the surface, Z_0 is the z component of the position vector $\mathbf{R}_0$ of the detector, σ^x, σ^y, σ^z are the usual Pauli spin matrices, and the

Pauli spinors χ_ν are eigenspinors of the spin projection $\sigma\cdot\hat{\mathbf{n}}$ along the direction n, specifying the orientation of the detector, with eigenvalues $\nu=\pm 1$. In terms of the relativistic LEED Green's function matrix[6] we may write

$$\langle \mathbf{r}|\psi_f^\nu\rangle = \langle r|G^-(\epsilon+\omega)|f,\nu\rangle. \tag{2}$$

A relativistic version of the usual arguments[5] leads to the following expression for the photocurrent:

$$I_{\nu,\nu}(\epsilon,\mathbf{k}_\parallel;\omega,\mathbf{q},\hat{\mathbf{a}},\hat{\mathbf{n}}) = -\frac{1}{\pi}\,\mathrm{Im}\langle f\nu|G^+(\epsilon+\omega)\Delta G^+(\epsilon)\Delta^+ G^-(\epsilon+\omega)|f\nu\rangle, \tag{3}$$

where $\mathbf{q}$ is the wave vector of the incident photon, $\hat{\mathbf{a}}$ is its polarization vector, $G(\epsilon)$ is the Green's function of the Dirac equation which describes the initial states of the photoemitted elements, and the interaction vertex Δ is given by

$$\Delta=\boldsymbol{\alpha}\cdot\hat{\mathbf{a}} \tag{4}$$

with the Dirac $\boldsymbol{\alpha}$ in the standard representation.[7]

Evidently, the direction $\hat{\mathbf{n}}$ is determined by the setting of the Mott detectors in the experiment.[3] For a given arrangement I_{++} and I_{--} are recorded separately. The spin-averaged photocurrent is $I=\frac{1}{2}(I_{++}+I_{--})$ and the polarization along $\hat{\mathbf{n}}$ is given by

$$\mathscr{P}\cdot\hat{\mathbf{n}} = (I_{++}-I_{--})/(I_{++}+I_{--}). \tag{5}$$

For an efficient theory of the Green's function $G^+(\epsilon+\omega)$, $G^-(\epsilon+\omega)$, $G(\epsilon)$ we follow the multiple-scattering apporach of Staunton, Gyorffy, and Weinberger.[8] The relevant scattering properties of each potential well are described by the partial-wave scattering amplitudes

$$-\epsilon^{1/2}t_\kappa(\epsilon) = (1/2i)\{\exp[i2\delta_\kappa(\epsilon)]-1\}$$

where $\delta_\kappa(\epsilon)$ are the phases shifts and κ is the spin-regular quantum number of the Dirac equation for spherically symmetric potentials. For clarity we note that $\kappa=-1,1,-2,2,-3,3$ corresponds to $l^j=s^{1/2}$, $p^{1/2}$, $p^{3/2}$, $d^{3/2}$, $d^{5/2}$, $f^{5/2}$, where l is the orbital polar and j is the total angular momentum quantum numbers. Multiple scattering between an arbitrary arrangement of scattering centers is described by the scattering-path matrix $\tau^{ij}_{\Lambda,\Lambda'}(\epsilon)$ where i and j refer to the sites at $\mathbf{R}_i$ and $\mathbf{R}_j$, respectively, and Λ stands for both κ and the magnetic quantum number m_j. It is a solution of the self-consistency equation

$$\sum_{i_2\Lambda_2}[t^{-1}_{i_1\Lambda_1}\delta_{i_1i_2}\delta_{\Lambda_1\Lambda_2}-G_{\Lambda_1\Lambda_2}(\mathbf{R}_{i_1}-\mathbf{R}_{i_2};\epsilon)]\tau^{i_2i_3}_{\Lambda_2\Lambda_3}(\epsilon)=\delta_{i_1i_3}\delta_{\Lambda_1\Lambda_3}, \tag{6}$$

where $G_{\Lambda\Lambda'}$ are the real-space relativistic Korringa-Kohn-Rostoker structure constants.[8] For $\mathbf{r}_i=\mathbf{r}-\mathbf{R}_i$ within the ith unit cell and $i\neq j$, we have

$$G(\mathbf{r}_i,\mathbf{r}_j;\epsilon)=\sum_{\Lambda\Lambda'}\psi_\Lambda(\mathbf{r}_i;\epsilon)\tau^{ij}_{\Lambda\Lambda'}(\epsilon)\psi_\Lambda(\mathbf{r}_j;\epsilon), \tag{7}$$

where $\psi_\Lambda(\mathbf{r};\epsilon)$ is the "regular" solution of the single-well Dirac equation. In terms of its large- and small-component radial solutions, $g_\kappa(r,\epsilon)$ and $f_\kappa(r,\epsilon)$, respectively, and the usual spin-angular spherical harmonics $\chi^{\omega_i}_H(\hat{\mathbf{r}})$,[7]

$$\psi_\Lambda(\mathbf{r};\epsilon)=\psi^{m_j}_\kappa(\mathbf{r};\epsilon)=\begin{pmatrix} g_\kappa(r;\epsilon)\chi^{m_j}_\kappa(\hat{\mathbf{r}}) \\ if_\kappa(r;\epsilon)\chi^{m_j}_{-\kappa}(\hat{\mathbf{r}})\end{pmatrix}. \tag{8}$$

To obtain the simple form of Eq. (7) we have chosen the normalization of g_κ and f_κ so that they match smoothly on to $\epsilon^{-1/2}t_k^{-1}j_l-ih_l$ and $\epsilon^{-1/2}t_\kappa^{-1}j_{l-S_\kappa}-ih_{l-S_\kappa}$, respectively, at the muffin-tin radius. As usual j_l is a spherical Bessel function, h_l is the corresponding Hankel function, and S_κ denotes the sign of κ.

For $i=j$ there is a correction to the right-hand side of Eq. (7). It is given by $\epsilon^{1/2}\Phi_\Lambda(\mathbf{r}_i;\epsilon)\psi_\Lambda(\mathbf{r}_i;\epsilon)$ where Φ_Λ is the "irregular" solution of the single-well Dirac equation corresponding to the "regular" solution given in Eq. (8).

In the case of a semi-infinite solid of interest here we also need the Green's function for $\mathbf{r}$ inside and $\mathbf{r}'$, outside the sample. In that case

$$G(\mathbf{r}_0,r_j;\epsilon)=\sum_{i\Lambda''\Lambda'''}\psi^0_\Lambda(\mathbf{r}_0;\epsilon)G_{\Lambda\Lambda''}(\mathbf{R}_0-\mathbf{R}_j;\epsilon)\tau^{ij}_{\Lambda''\Lambda'''}\psi_{\Lambda''}(\mathbf{r}_i;\epsilon)$$

where $\mathbf{R}_0$ is a point inside the sample, the detector's position for instance, and ψ^0_Λ is the solution of the free-particle Dirac equation with large component $g^0_\kappa=j_l$ and small component $f^0_\kappa=j_{l-S_\kappa}$.

Using the above general results we may evaluate the right-hand side of Eq. (3) to obtain

$$I_{\nu\nu} = I_s + I_{\rm at} - \frac{1}{\pi}\,{\rm Im}\sum_{\{i\}}\sum_{\{\Lambda\}} f^{\nu}_{\Lambda_1}(\epsilon+\omega)\,G_{\Lambda_1\Lambda_2}(\mathbf{R}_0-\mathbf{R}_{i_1};\epsilon+\omega)\,\tau^{i_1 i_2}_{\Lambda_2\Lambda_3}(\epsilon+\omega)\,M^{i_2}_{\Lambda_3\Lambda_4}(\epsilon,\omega)\,\tau^{i_2 i_3}_{\Lambda_4\Lambda_5}(\epsilon)$$
$$\times M^{i_3}_{\Lambda_5\Lambda_6}(\epsilon,\omega)\,\tau^{i_3 i_4}_{\Lambda_6\Lambda_7}(\epsilon+\omega)\,G_{\Lambda_7\Lambda_8}(\mathbf{R}_{i_4}-\mathbf{R}_0;\epsilon+\omega)\,f^{*\nu}_{\Lambda_8}(\epsilon+\omega), \tag{9}$$

where I_s is a surface term, and the atomic term $I_{\rm at}$ arises from the single-site contribution to the site-diagonal part of the low-energy Green's function. $f^{\nu}_{\Lambda} = \langle f_{\nu}|\psi^0_{\Lambda}\rangle$ and $M^{i}_{\Lambda\Lambda'}$ is a single-site dipole matrix element. For the relativistic version of the acceleration formula we find

$$M_{\Lambda\Lambda'}(\epsilon,\omega) = \langle\psi_{\Lambda}(\epsilon)|\boldsymbol{\alpha}\cdot\hat{\mathbf{a}}|\psi_{\Lambda'}(\epsilon+\omega)\rangle$$
$$= \frac{2ic}{[2(\epsilon+C^2)+\omega]\omega} D_{\Lambda\Lambda'}\int dr\, r^2\left\{\frac{\partial V}{\partial r}(g_{\kappa}g_{\kappa'}+f_{\kappa}f_{\kappa'}) - \frac{i\omega}{c}V[g_{\kappa}f_{\kappa'}(\kappa'-\kappa-1)+f_{\kappa'}g_{\kappa}(\kappa'-\kappa+1)]\right\}, \tag{10}$$

where the angular part which contains the polarization of the incident photons is given by

$$D_{\Lambda,\Lambda'} = \int d^2\hat{r}\,\chi^{*}_{\Lambda}(\hat{\mathbf{r}})\hat{\mathbf{a}}\cdot\hat{\mathbf{r}}\chi^{t}_{\Lambda'}(\hat{\mathbf{r}}). \tag{11}$$

In this theory the usual selection rules are $\kappa' = -\kappa$, or $\kappa \pm 1$, and $m_j + m_j' = 0$. The unconventional form of the latter is due to the fact that the axis of quantization in the final state is taken to be in the opposite direction to that in the initial state. For $C \to \infty$ the above formulas reduce to those of the nonrelativistic theory as presented by Durham.[9] Further details will be published elsewhere.

We have implemented the calculations implied by Eq. (9) using the layer method[5,9] for the experimental geometry considered by Eyers *et al.*[3]: normally incident circularly polarized photons and electrons emitted along the surface normal. In order that our calculations would correspond to their measurements we have taken the direction of our "gedanken" detector n to be also normal to the surface. The one-electron potential function we have used was obtained in a self-consistent linear combination of muffin-tin orbitals (LMTO) calculation. We have also calculated fully relativistic energy bands by the layer method.[10] As regards the d bands, they agree with our LMTO calculations to within a few millirydbergs. Since the latter were solutions of the (linearized) Pauli equation, this level of agreement is satisfactory. This constitutes an important check of our programs for the low-energy states. Furthermore, in the $C \to \infty$ limit our layer-method bands agreed essentially exactly with those of a nonrelativistic Kerringa-Kohn-Rostoker calculation, as they should. The corresponding photocurrents also agreed excellently with the results of a separate nonrelativistic program.[5] A final test is to calculate the spin polarization of the photocurrent for linearly polarized light—this was found to vanish, in accordance with

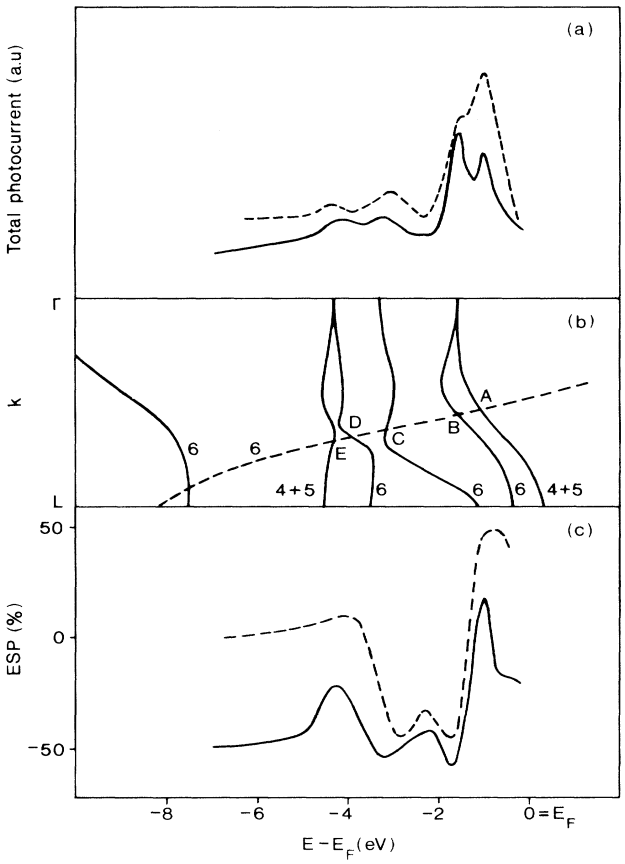

FIG. 1. (a) Normal incidence, normal emission spectrum ($h\omega = 14$ eV) for Pt(111); theory (full line), experiment (Ref. 3) (dashed line). (b) Energy bands in the Λ direction. The dashed curve is the final-state band moved down in energy by 14 eV. Direct transitions can occur at the intersections A–E. (c) Electron spin-polarization spectrum for the right-hand circularly polarized radiation; theory (full line), experiment (Ref. 3) (dashed line).

symmetry requirements. For a normal-incidence, normal-emission experiment the spin polarization parallel to the surface should be zero even for circularly polarized light. Our calculations obeyed this rule.

In Fig. 1 we compare our theoretical photocurrent with that obtained by Eyers *et al.*[3] In view of the fact that this is the first relativistic calculation of the photocurrent it is of interest that the two high-binding-energy peaks can be unambiguously assigned to transitions from the spin-orbit-split Λ_{4+5} and Λ_6 bands. A comparison of these peaks with the experimental curve suggests that this splitting may be too small, and their relative intensities are somewhat in error. Overall, however, the peak positions and intensities are in very satisfactory agreement with the data.

Our central result is the spin polarization $\mathscr{P}_z = (I_{++} - I_{--})/(I_{++} + I_{--})$ shown, together with the experimental data, on the lower panel of Fig. 1. Our calculation reproduces the approximately 50% observed values quite accurately at low binding energies. At higher binding energies the agreement is only qualitative. Note that the data contain a background of (presumably) unpolarized secondary electrons, rising with increasing binding energy. This is, of course, absent in our calculations, making comparison rather difficult in this energy range. We attribute the very satisfactory overall description of the polarization by the theory to the adequate treatment of the matrix elements and the hybridization effects, in addition to a correct account of symmetry.

We now comment on the origin of the spin polarization of the photocurrent. If we neglect the surface and assume a direct transition model, it is straightforward to adapt the atomic calculation of Fano[4] to give a qualitative discussion of the present case.[11] Within each cell we write the initial and final states as Bloch sums:

$$\langle \mathbf{r}|i\rangle = \frac{1}{\sqrt{N}} \sum_{\substack{n,L,\\ s}} b_{L,s}^{(i)}(\mathbf{k}) \phi_{L,s}^{(i)}(\mathbf{r}-\mathbf{R}_n) \exp(i\mathbf{k}\cdot\mathbf{R}_n),$$

$$\langle \mathbf{r}|f\rangle = \frac{1}{\sqrt{N}} \sum_{\substack{n,L,\\ s}} b_{L,s}^{(f)}(\mathbf{k}) \phi_{L,s}^{(f)}(\mathbf{r}-\mathbf{R}_n) \exp(i\mathbf{k}\cdot\mathbf{R}_n),$$

where $\mathbf{R}_n$ is a lattice vector and $\phi_{L,S}^{(i,f)}$ an "atomic" orbital of angular momentum $L\,(=l,m)$ and spin S. The spin polarization can be expressed in terms of "atomic" dipole matrix elements linking ϕ^f and ϕ^i, and of the band coefficients $b_{L,s}^{(i)}(\mathbf{k})$ and $b_{L,s}^{(f)}(\mathbf{k})$. We use Fig. 1 to locate transitions in $\mathbf{k}$ space, and our LMTO band calculation to find the corresponding coefficients $b^{(i,f)}$. Then, using the selection rules and assuming the $d \rightarrow p$ matrix element to be dominant, we find polarization of 47%, −37%, 33%, −49%, and 71%, respectively, for transitions A–E. This estimate agrees sufficiently well with experiment and with the full calculation for us to conclude that the spin polarization spectrum is indeed largely determined by the spin character of the bands, as described by the coefficients $b^{(i,f)}(\mathbf{k})$. It is most interesting to obtain such information on Pt, but one can easily imagine systems whose magnetic behavior is controlled by the interplay of spin-orbit and exchange coupling (e.g., Ni-Pt compounds and alloys,[12] rare earths, etc.). For such systems the spin-polarization spectrum will be a vital probe.

Finally we note that on the basis of the above calculations we would expect significant polarization effects in an inverse-photoemission experiment where the final (empty) state is a strongly spin-orbit-split state, even if the polarization of the emitted photon is not detected. That such empty states exist in Pt is known from x-ray absorption measurements. Evidently this phenomenon could be used as a basis for a detector of the spin polarization of low-energy electron beams.

[1]R. H. Williams, G. P. Srivastava, and I. T. McGovern, Rep. Prog. Phys. **43**, 1357 (1980).

[2]E. Kisker, K. Schroder, M. Campagna, and W. Gudat, Phys. Rev. Lett. **52**, 2285 (1984).

[3]A. Eyers, F. Schafers, G. Schnonhense, U. Heinzmamann, P. Oepen, K. Hunlich, J. Kirschner, and G. Borstel, Phys. Rev. Lett. **52**, 1559 (1984).

[4]U. Fano, Phys. Rev. **178**, 131 (1969), and **184**, 250 (1969); see also N. A. Cherepkov, J. Phys. B **12**, 1279 (1979).

[5]J. B. Pendry, Surf. Sci. **57**, 679 (1976); also J. F. L. Hopkinson, J. B. Pendry, and D. J. Titterington, Comput. Phys. Commun. **19**, 69 (1980).

[6]A. P. Shen, Phys. Rev. B **9**, 1328 (1976).

[7]M. E. Rose, *Relativistic Electron Theory* (Wiley, New York, 1961).

[8]J. Staunton, B. L. Gyorffy, and P. Weinberger, J. Phys. F **10**, 2665 (1983).

[9]P. J. Durham, in *Electronic Structure of Complex Systems,* edited by P. Phariseau and W. Temmerman (Plenum, New York, 1984).

[10]J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974).

[11]See also R. Allenspach, F. Meier, and D. Peschia, Phys. Rev. Lett. **51**, 2148 (1983); M. Wohlecke and G. Borstel, Phys. Rev. B **23**, 980 (1981).