Peak rotation in photoelectron diffraction patterns by circularly polarized light

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Forward-scattering peaks in the angular distribution of photoelectrons rotate for a dominant angular and magnetic quantum number pair $L_0 = (l_0, m_0)$ in the direct wave. This rotation is explained within the quantum-mechanical scattering theory. The result is an extension of the model of Daimon *et al.* [Jpn. J. Appl. Phys. **32**, L1480 (1993)] who use a semiclassical picture of motion. An approximate formula is derived within the single-scattering approximation. It is shown that the phase of the scattering amplitude at forward scattering determines whether there is a maximum or a minimum in the intensity. [S0163-1829(97)02007-9]

I. INTRODUCTION

Forward-scattering peaks in photolectron diffraction (PD) spectra occur when photoelectrons emitted with kinetic energies of several hundred eV are scattered by atoms around the emitting atom. This scattering process produces enhanced intensities in the directions connecting the emitting atom with its overlying nearest and next-nearest-neighbor atoms.[1–3]

Daimon *et al.*[4,5] measured the angular distribution of Si 2*p* core-level photoelectrons in Si(001) with right and left circularly polarized light entering normal to the surface. The experiment involved kinetic energies from 150 to 450 eV. A rotational shift of forward-scattering peaks was observed in the photoelectron diffraction pattern. The peaks rotate in the same direction as the rotational direction of the electric field vector of light. It was proposed that this rotation induces the observed strong circular dichroism in the angular distribution (CDAD) of photoelectrons in Si(001). This type of CDAD differs to the usual CDAD in molecules and nonmagnetic solids[6] since the interaction of the photoelectron with the substrate cannot be neglected.[7]

There have been several attempts to explain the rotational shift of forward-scattering peaks and therefore this type of CDAD. Daimon interpreted the rotation of peaks by considering the dipole selection rules for circularly polarized light, without considering the scattering process in detail. If the emitted electron wave has a dominant component with a nonzero magnetic quantum number m_0 the wave fronts hitting a scatterer are rotated by a certain angle. The forward-scattering direction then is rotated in the same manner. Kaduwela *et al.*[8] applied a multiple-scattering formalism[9] based on the Rehr-Albers approximation[10] to explain CDAD in Si(001). It was shown by numerical evaluation that photoelectron diffraction theory can quantitatively explain the peak rotation with change in light polarization. A good agreement between theory and experimental results of Daimon *et al.*[4] has been reached. In a recent theoretical study by Fujikawa and Yimagawa[11] CDAD of nonmagnetic materials was discussed on a multiple-scattering cluster method. For the excitation of 1*s* core-level photoelectrons by right and left circularly polarized light a formula of rotational shift was derived that fails to explain the correct angle of rotation.

In this work a straightforward quantum-mechanical inter-

pretation of the peak rotation will be presented. It is shown that the simple formula of Daimon *et al.*[4] can be derived by considering forward-scattering effects in photoemission to a single component of the direct wave. In Sec. II the basic formulas of a photoelectron diffraction theory based on the full angular momentum expansion are summarized. The rotation of forward-scattering peaks is described in Sec. III. It is shown that the formula of Daimon *et al.*[4] follows in the single-scattering approximation directly. As an example theoretical results are shown for Si $2p_{1/2}$ core-level photoelectrons in Si(001). Section IV contains conclusions.

II. THEORY

The intensity of emitted core-level photoelectrons depends on the emission direction ($\mathbf{k} = k\hat{\mathbf{k}}$), the photoelectron spin (quantum number σ), the kinetic energy ($E = \hbar^2 k^2 / 2m$), and the photon polarization $\vec{\epsilon}$ (Ref. 12)

$$I_c^\sigma(\mathbf{k}, \vec{\epsilon}) \sim \sum_{\mathbf{R}_0} \sum_{\mu_c} \left| \sum_L B_L^{\sigma, \mathbf{R}_0}(\mathbf{k}) M_{L,c}^\sigma(E, \vec{\epsilon}) \right|^2. \quad (1)$$

The sums in Eq. (1) run over all contributions of different atoms $\mathbf{R}_0$ where the photon is absorbed creating a hole state c with a degeneracy μ_c. The letter L is an abbreviation for the angular quantum number l and its related magnetic quantum numbers m of the photoelectron. M in Eq. (1) represents the dipole matrix element

$$M_{L,c}^\sigma(E, \vec{\epsilon}) = \exp(i\delta_l^*) \langle \phi_l | r | \phi_{j_c l_c} \rangle \langle L\sigma | \hat{\mathbf{r}} \cdot \vec{\epsilon} | j_c l_c \mu_c \rangle. \quad (2)$$

The core state c is split by the spin-orbit interaction and its spin and angular part $|c\rangle = |j_c l_c \mu_c\rangle$ is characterized by the total angular quantum number j_c, the angular quantum number l_c, and the related magnetic quantum number μ_c. From the part $\langle L\sigma | \hat{\mathbf{r}} \cdot \vec{\epsilon} | j_c l_c \mu_c \rangle$ in Eq. (2) it follows which (l,m) values contribute to the intensity Eq. (1). Within the dipole approximation only the values $l = l_c \pm 1$ are allowed. The radial part $R_l = \exp(i\delta_l^*) \langle \phi_l | r | \phi_{j_c l_c} \rangle$ in Eq. (2) determines the weight of the partial waves with quantum numbers $l = l_c \pm 1$. In Eq. (2) δ_l^* is the scattering phase shift of the excited atom.
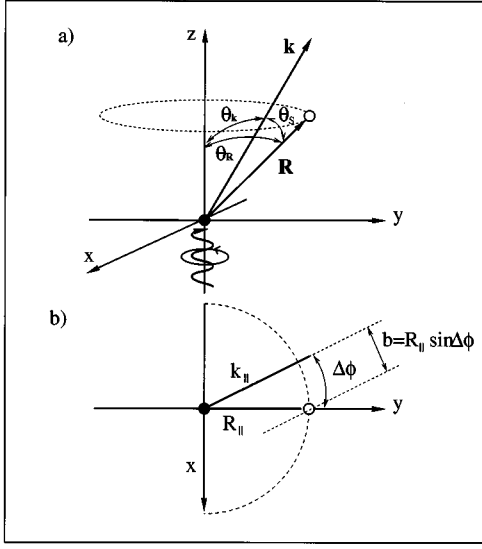
FIG. 1. Schematic illustration of the azimuthal rotation of photoelectrons excited by right circularly polarized light.

The scattering path operator in Eq. (1) (Ref. 13)

$$B_L^{\sigma,\mathbf{R}_0}(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{R}_0}(-i)^l Y_L(\hat{\mathbf{k}}) + \sum_{\mathbf{R}'\neq\mathbf{R}_o}\sum_{L'} e^{-i\mathbf{k}\cdot\mathbf{R}'}$$

$$\times (-i)^{l'} Y_{L'}(\hat{\mathbf{k}})(-ikt_{l'}^{\sigma})G_{L'L}(\mathbf{R}'-\mathbf{R}_0)$$

$$+ \sum_{\mathbf{R}''\neq\mathbf{R}'}\sum_{\mathbf{R}'\neq\mathbf{R}_0}\sum_{L''}\sum_{L'} e^{-i\mathbf{k}\cdot\mathbf{R}''}(-i)^{l''}Y_{L''}(\hat{\mathbf{k}})$$

$$\times (-ikt_{l''}^{\sigma})G_{L''L'}(\mathbf{R}''-\mathbf{R}')(-ikt_{l'}^{\sigma})$$

$$\times G_{L'L}(\mathbf{R}'-\mathbf{R}_0) + \cdots \tag{3}$$

describes the direct wave (first term), the single (second term) and multiple-scattering contributions. The single site scattering matrix element t_l in Eq. (3) is defined as $t_l = -k^{-1}\exp(i\delta_l)\sin\delta_l$. The scattering phase shifts δ_l for the different kinds of atoms depend on the kinetic energy of the photoelectrons and, for magnetic materials, on the spin σ. $G_{L'L}$ is the matrix element of the Greens operator[14] and Y_L represents the spherical harmonic of the first kind.[15]

III. ROTATION OF FORWARD-SCATTERING PEAKS

We consider the scattering path operator (3) for an emitter at the origin and one scattering atom at the position $\mathbf{R}$ ($=R\hat{\mathbf{R}}$) [Fig. 1(a)]. The matrix elements $G_{L'L}$ in Eq. (3) are replaced by their asymptotic expression[13] [$kR\gg l(l+1)$]

$$G_{L'L}(\mathbf{R}) \approx 4\pi(-i)^{l-l'}\frac{e^{ikR}}{ikR}Y_{L'}^*(\hat{\mathbf{R}})Y_L(\hat{\mathbf{R}}). \tag{4}$$

The scattering path operator for this simple example can be written in the approximate form

$$B_L(\mathbf{k}) \approx (-i)^l Y_L(\hat{\mathbf{k}}) + \frac{e^{ikR(1-\cos\theta_s)}}{R}f(\theta_s)(-i)^l Y_L(\hat{\mathbf{R}}), \tag{5}$$

where $f(\theta_s)$ is the complex scattering amplitude

$$f(\theta_s) = -4\pi\sum_{L'} t_{l'}Y_{L'}(\hat{\mathbf{k}})Y_{L'}^*(\hat{\mathbf{R}})$$

$$= -\sum_{l'=0,1,\ldots}(2l'+1)t_{l'}P_{l'}(\cos\theta_s). \tag{6}$$

For the second equation in Eq. (6) we used an addition formula for the spherical harmonics.[15] The Legendre polynomial P_l in Eq. (6) depends on the scattering angle θ_s, which is the angle between the direction of the observer $\hat{\mathbf{k}}$ and the axis between emitter and scattering atom $\hat{\mathbf{R}}$ [Fig. 1(a)]. The cosine of θ_s can be expressed with the polar (θ) and azimuthal angles (ϕ) of $\hat{\mathbf{k}}$ and $\hat{\mathbf{R}}$, respectively

$$\cos\theta_s = \cos(\phi_k-\phi_R)\sin\theta_k\sin\theta_R + \cos\theta_k\cos\theta_R. \tag{7}$$

The spherical harmonic of the first kind $Y_L(\hat{\mathbf{x}})$ in Eq. (5) depends on the polar and azimuthal angle of the unit vector $\hat{\mathbf{x}}$,

$$Y_L(\hat{\mathbf{x}}) = Y_L(\theta_x,\phi_x) = N_L P_L(\cos\theta_x)e^{im\phi_x} \tag{8}$$

and contains the real associated Legendre function P_L.[15] N_L in Eq. (8) is the normalization constant.

We consider a dipole transition where one of the quantum number pair $L\equiv L_0 = (l_0,m_0)$ in Eq. (1) dominates all the others contributions. Therefore the intensity (1) is proportional to $|B_{L_0}|^2$, which follows from Eq. (5):

$$|B_{L_0}|^2 = |N_{L_0}|^2\bigg\{P_{L_0}^2(\cos\theta_k) + P_{L_0}^2(\cos\theta_R)|f(\theta_s)|^2\frac{1}{R^2}$$

$$+ P_{L_0}(\cos\theta_k)P_{L_0}(\cos\theta_R)|f(\theta_s)|\frac{2}{R}$$

$$\times\cos[m_0(\phi_k-\phi_R)-kR(1-\cos\theta_s)-\psi(\theta_s)]\bigg\}. \tag{9}$$

In Eq. (9) $\psi(\theta_s)$ is the phase of the complex scattering amplitude $f(\theta_s)$ [Eq. (6)].

The azimuthal rotation of forward-scattering peaks follows in our calculation straightforwardly. We determine the maximum of the intensity (1) for fixed values $\theta_k = \theta_R \equiv \theta$ in dependence on $\Delta\phi = \phi_k - \phi_R$. The phase and absolute value of the scattering amplitude are approximated by the values at $\theta_s = 0°$. Further we assume that the difference between both azimuthal angles $\Delta\phi$ is small. We expand $\cos\Delta\phi$ in Eq. (7) in a series of $\Delta\phi$ up to the second order and get $\cos\theta_s \approx 1 - \frac{1}{2}(\Delta\phi)^2\sin^2\theta$. The derivative of Eq. (9) with respect to $\Delta\phi$,

$$\frac{\partial}{\partial\Delta\phi}|B_{L_0}|^2 = -|N_{L_0}|^2 P_{L_0}^2(\cos\theta)|f(0)|\frac{2}{R}$$

$$\times\sin\bigg[m_0\Delta\phi - \frac{1}{2}kR(\Delta\phi)^2\sin^2\theta - \psi(0)\bigg]$$

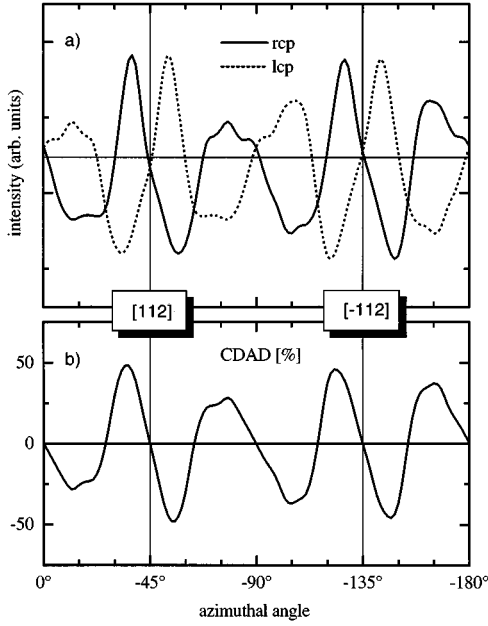$$\times(m_0 - kR\Delta\phi\sin^2\theta) \tag{10}$$

vanishes for

FIG. 2. Total intensity (a) and CDAD (b) of Si $2p_{1/2}$ core-level photoelectrons from the Si(001) surface in dependence on the azimuthal angle ϕ (Ref. 18) for $\widetilde{\theta}=35.3°$. The photoelectron energy is 250 eV. The intensity has been calculated within the full angular momentum representation (3), taking into account single-scattering processes. Data are shown for 100% circularly polarized light.

$$\Delta\phi=\frac{m_0}{kR\sin^2\theta}. \qquad (11)$$

The formula (11) gives a maximum for

$$\psi(0)>\frac{m_0}{2}\Delta\phi=\frac{1}{2}\frac{m_0^2}{kR\sin^2\theta}. \qquad (12)$$

For $\psi(0)<\frac{1}{2}m_0\Delta\phi$ we find a local minimum at $\Delta\phi$ given by Eq. (11), whereas there is a maximum at values $\Delta\phi$ where the argument of the sine in Eq. (10) vanishes. The expression given in Ref. 11 gives the position of a maximum in the special case of $\psi(0)=0$ and therefore it fails in the description of the observed peak positions. Equation (12) shows that the condition for the maximum is independent on the sign of m_0.

The simple formula (11) can be interpreted as an azimuthal rotation of the forward-scattering direction as introduced by Daimon et al.[4] When the scattering atom exists at (R,θ,ϕ) from the emitting atom, the forward-scattering peak appears in the direction $(\theta,\phi\pm\Delta\phi)$ as shown in Fig. 1(b).

In a classical picture of the scattering process the angular momentum L is the product of the momentum p $(=\hbar k_{||})$ and the impact parameter b $(=R_{||}\sin\Delta\phi)$ [Fig. 1(b)]. From $L=bp=\hbar m_0$ we find the condition (11).

In Fig. 2 theoretical results are shown for the Si $2p_{1/2}$ core level in Si(001). The calculations have been done for a cluster of 46 Si atoms at the Si(001) surface including emitters in the first five layers. The energy of photoelectrons amounts $E=250$ eV. The scattering phase shifts δ_l and the radial matrix elements R_l have been calculated in the usual way from a muffin-tin model of the Si bulk using Mattheiss

construction[16] and an X_α exchange potential. The scattering path operator (3) has been taken within the full angular momentum expansion restricted to single scattering contributions. In Fig. 2(a) the intensity of photoelectrons excited by right (rcp) and left (lcp) circularly polarized light are shown in dependence on the azimuthal angle ϕ for the emission angle $\widetilde{\theta}=35.3°$ with respect to normal electron emission. The vertical thin lines correspond to forward-scattering directions for an emitter in the fifth layer and a scatterer in the first one. We get an azimuthal shift $\Delta\phi$ of the [112] and [$\bar{1}$12] peaks of 8°. The shift is opposite for rcp and lcp light, respectively. In Fig. 2(b) the CDAD $D(\phi)$ is shown. It reflects the symmetry relations $D(\phi)=D(\phi+180°)$ and $D(\phi_0+\phi)=-D(\phi_0-\phi)$, which can be derived from the symmetry of the Si(001) surface, where $\phi_0=45°,135°$ are the positions of the mirror planes of this surface.

In the considered energy region the dipole transition to $l=2$ is much more probable than to $l=0$ because the squared ratio of the radial matrix elements is about 14. This is well known for p-level photoelectrons with energies well above threshold[17]. For rcp light the square of the angular and spin part of the matrix element (2) is $\frac{4}{15}$, $\frac{2}{15}$, $\frac{2}{45}$ for $m=2,1,0$, respectively and vanishes for $m=-1,-2$. Therefore, the $m=\pm2$ partial wave of the final state should dominate for rcp and lcp light, respectively. The predicted azimuthal shift $\Delta\phi$ for the two peaks using formula (11) amounts to $\pm6.4°$.

If we restrict our calculation to the $L=(2,2)$ partial wave for rcp light, one emitter, and one scatterer then we get the predicted value determined by Eq. (11). However, the azimuthal shift $\Delta\phi$ depends on both the other m values and the scattering contributions from the other atoms in the cluster. If we add the intensities for emitters in all layers then we get $\Delta\phi=8°$ which is seen in Fig. 2(a).

Formula (12) determines whether there is a maximum or a minimum of the intensity (1) at $\Delta\phi$ (11). Therefore we have calculated $\psi(0)$ in dependence on the energy of the photoelectron. In the range between 100 and 300 eV $\psi(0)$ varies between 0.9 and 0.7. For $|m_0|=2$ and $\Delta\phi=6.4°$ we have $\Delta\phi m_0/2\approx0.1$. Thus Eq. (12) is satisfied in the considered energy range, we always find a maximum of the intensity.

IV. CONCLUSIONS

We have shown that the rotational shift of forward-scattering peaks in photoelectron diffraction patterns can be explained straightforwardly within the quantum-mechanical scattering theory. An approximate formula has been derived within the single-scattering model through which the physically intuitive explanation due to Daimon et al.[4,5] has been proved. It seems to be a good approximation to predict the magnitude and the direction of the rotational shift. The phase $\psi(0)$ of the scattering amplitude at forward scattering determines whether there is a maximum or minimum.

In order to reconstruct the observed peak positions precisely, however, we need a calculation including the full final state of photoelectrons. Detailed investigations[8] and our discussion in Sec. III show that the azimuthal shift of forward-scattering peaks $\Delta\phi$ in the pattern of bulk PD is determined by several contributions.

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[18] The azimuthal angle in this figure is with respect to the coordinate system in Fig. 1, through which the photon wave vector is opposite to the normal electron emission direction.