Symmetry-dependent alignment of the electron-spin polarization vector due to electronic band hybridization observed in photoemission from Ag(100)

C. M. Schneider, J. Garbe, K. Bethke, and J. Kirschner
Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich, Postfach 1913, D-5170, Jülich, Federal Republic of Germany
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We have performed spin- and angle-resolved photoemission experiments in normal emission from a (100) surface of silver using circularly polarized synchrotron radiation at oblique and normal incidence. The observed spin polarization reaches values up to 45%, with the corresponding peaks in the intensity distributions fully consistent with the bulk band structure. In the case of normally incident light the spin polarization vector is aligned with the surface normal, whereas deviations from this behavior are found at oblique incidence of the circularly polarized light. A particular hybridization in the initial states is responsible for this effect, which can be understood on the base of symmetry arguments.

I. INTRODUCTION

It has been demonstrated in recent years that a number of important details in the experimental band structure of nonmagnetic solids may only be understood by taking into account the effects of spin-orbit coupling. Most of these results were obtained by spin- and angle-resolved analysis of photoelectrons excited with circularly polarized light from (111) and (110) transition-metal surfaces.[1,2] For several reasons a particular, highly symmetric geometry was chosen for these experiments. In this arrangement the wave vector $\mathbf{k}_p$ of the incident photon is aligned with the surface normal and only the normally emitted electrons ($\mathbf{k}_{\parallel} \approx \mathbf{0}$) are detected. Supposing completely circular-polarized light, the existence of at least two mirror planes perpendicular to the surface then leads to a spin-polarization vector with a nonzero component only along the surface normal.[3] This setup also provides the advantage of correlating the spin-polarization vector inside the crystal directly with the measured one, because no alteration is introduced by the transmission step. Furthermore the degree of circular polarization of the incident light is preserved inside the solid. By means of relativistic selection rules this geometry immediately allows one to determine the symmetries and possible hybridizations of the initial states involved in the specific transitions by the sign and magnitude of the spin polarization.

The orientation of the spin-polarization vector is intimately connected to the symmetry of the system. It is essential that the relevant symmetry is not only determined by the surface under investigation, but must include the incident photon and the emitted electron as well. For example, the detection of off-normally emitted electrons ($\mathbf{k}_{\parallel} \neq \mathbf{0}$) means a lower symmetry of the whole system compared to normal emission, a fact that lifts the above-mentioned restrictions on the orientation of the polarization vector,[4] and even results in an asymmetric behavior of the observed intensities when switching the helicity of the light.[5] Also, the lack of space inversion symmetry due to the existence of the surface itself (a fact generally not considered within the three-step model) may lead in the particular case of a (111) surface to an orientation of the spin-polarization vector other than parallel to the surface normal.[6] However, this latter effect may only be observed by excitation with linearly polarized light, but vanishes for light which is completely circular polarized.

A different way of lowering the symmetry of the system is achieved by detecting the normally emitted electrons, but moving the direction of incidence of the light away from the surface normal. This geometry is frequently involved in photoemission with linearly polarized light to distinguish between initial states of different parity with respect to a mirror plane via the distinctive excitation by *s*- or *p*-polarized radiation. In principle this concept is valid only if the effects of spin-orbit coupling can be neglected and a purely spatial symmetry classification of the electronic bands is justified. Therefore a clear-cut determination of the symmetries of spin-orbit-split bands on the basis of parity analysis is impossible. Yet the question arises as to whether this experimental variant, applied in spin-resolved photoemission with circularly polarized light, may reveal some new information on the electronic states which is not attainable from normal-incidence experiments. In particular, this could be expected if the orientation of the spin-polarization vector at obliquely incident light deviates from the surface normal. The following mechanisms may give rise to such a behavior. On the one hand, the direction of the wave vector $\mathbf{k}_p$ in the crystal may define a new quantization axis, which is inclined to the surface normal. Then only spin-polarization vectors parallel or antiparallel to a fixed direction in space (which is not the surface normal) should be found. On the other hand, the component of the vector potential perpendicular to the surface may excite additional transitions, which do not occur in the case of normal incidence. This should lead to a transition-dependent orientation of the spin-polarization vector, which means that polarization vectors involving different types of transition may be aligned with different directions in space.

II. EXPERIMENTAL ASPECTS

The spin-polarized photoemission experiments were conducted at the German storage ring of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) with elliptically polarized light using the apparatus described in detail elsewhere.[1] The sample was a silver single crystal cut parallel to a (100) plane within an accuracy of 0.5°. Prior to insertion in the vacuum it was etched and polished by standard procedures. The surface was prepared by repeated cycles of sputtering with argon ions and subsequent annealing. This treatment was continued until the examination by Auger-electron analysis and the low-energy electron diffraction (LEED) pattern indicated a clean, well-ordered surface. The good structural condition of the sample was also confirmed by the quality of the electron-channeling patterns. These were obtained by scanning the electron beam from the Auger system over the sample surface and modulating synchronously the intensity of a TV monitor with a voltage proportional to the sample current. The contrast in these geometrical patterns arises from anomalous absorption or channeling effects and depends on the inclination of the incident electron beam relative to the Bragg planes of the crystal. After preparation the crystal is transferred in the adjacent experimental chamber containing the electron spectrometer with the LEED detector for spin-polarization analysis. The latter allows the simultaneous measurement of two orthogonal components of the spin-polarization vector, one being parallel to the wave vector $\mathbf{k}_e$ of the emitted electron, the other one perpendicular to the electron momentum. To vary the angle of incidence, the sample was rotated about an axis perpendicular to the plane of the storage ring, which was identical with the rotational axis of the spectrometer. In this way, the detection of normally emitted electrons could be achieved for each angle of incidence.

The symmetry of the silver (001) surface (and the Δ direction normal to it) is described by the C_{4v} point group. It contains two sets of orthogonal mirror planes rotated relative to each other by $\pi/4$: {(010),(001)} and {(110),(110)}. To simplify the interpretation of the results the (110) mirror plane ($\Gamma KLUX$) of the crystal was oriented parallel to the plane of the storage ring. In this geometry the components of the spin-polarization vector normal to the surface (P_{long}) and parallel to the $\Gamma KLUX$ plane (P_{trans}) can be measured. The spectra were recorded for both negative and positive helicity of the circularly polarized light in order to eliminate the apparatus asymmetry of the spin detector.

III. RESULTS

A. Normal incidence

First we have measured the intensity and spin-polarization spectra of the normally emitted electrons for normally incident light. In this highly symmetric geometry a nonzero component of the spin-polarization vector only parallel to the surface normal is allowed. As mentioned above this is due to the existence of two mirror planes which contain the surface normal and the direction of incidence. The results for a photon energy of $h\nu = 12.5$ eV are displayed in Fig. 1. The spectrum is combined from the corresponding spectra of opposite helicity, each corrected for a constant background. At binding energies of $E_B = -4$ and -4.3 eV the intensity distribution [Fig. 1(a)] shows weakly resolved structures, whereas in the spin-polarization component along the

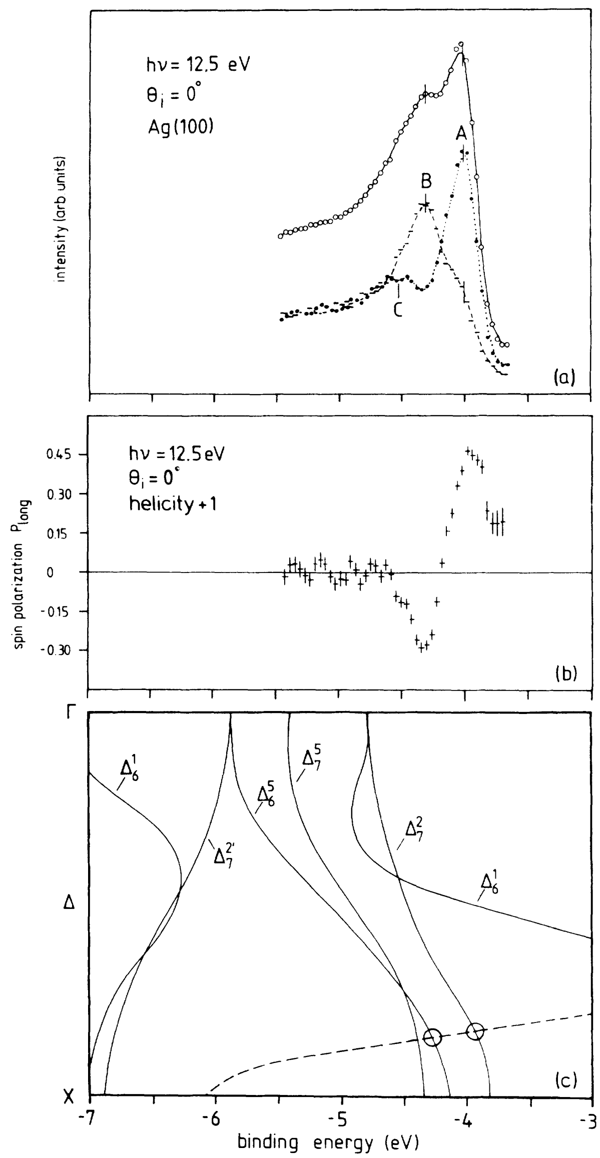

FIG. 1. (a) Energy-distribution curve and (b) spin polarization of the normally emitted electrons at normally incident light with $h\nu = 12.5$ eV. Partial intensities corresponding to a spin polarization vector parallel (· · · ·) and antiparallel (— — —) to the surface normal are additionally indicated in (a). The relevant section of the band structure (Ref. 7) with the Δ_6^1 final-state band (— — —) shifted down by $h\nu$ is given in (c).

surface normal [Fig. 1(b)] a strong feature appears, going from $+45\%$ to -30%. In this particular geometry, where the spin polarization may be considered as scalar, just having a positive or negative value, a decomposition into partial intensities is applicable. These partial intensities, calculated according to $I_{\pm}=(I/2)(1\pm P)$, therefore exhibit the resolved peaks correlated to the polarization vector parallel ($\cdots$) and antiparallel (— — —) to the surface normal. Additionally a weak peak (labeled C) at $E_B=-4.5$ eV becomes visible.

These features may be fully interpreted in terms of direct transitions within the bulk band structure using relativistic selection rules. Along the Δ-symmetry line only the doubly degenerate Δ_5 band (single-group representation) splits due to spin-orbit coupling into bands with the symmetries of the corresponding double-group representations Δ_6^5 and Δ_7^5. This notation for double-group representations uses the conventional symbol for a special axis in the Brillouin zone (Δ) and the standard Bouckaert-Smoluchowski-Wigner designation of the single group as a superscript and of the double group as a subscript. In the chosen geometry the vector potential $\mathbf{A}$ of the incident light is perpendicular to the surface normal, so only the following transitions are allowed to occur[3]

$$\begin{array}{l}\Delta_6^5\rightarrow\Delta_6^1\\ \Delta_7^5\rightarrow\Delta_6^1\end{array}\quad(\mathbf{A}\|x,\ \mathbf{A}\|y)\ . \tag{1}$$

These optical transitions may be excited either with linearly polarized light both along x or along y (the z axis being parallel to the surface normal) or with circularly polarized light. But only in the latter case the excitation yields spin-polarized photoelectrons.

According to the sign of the spin polarization peak A arises from a transition starting from a band of Δ_7^5 symmetry, and peak B is related to a Δ_6^5-like initial state. The spin-orbit splitting of these bands is equal to the difference in binding energies and is determined to $\Delta E_{\mathrm{s.o.}}=300$ meV at this particular $\mathbf{k}$ value of the bulk Brillouin zone (BZ). These results agree well with a relativistic band-structure calculation given by Eckardt *et al.*,[7] which is also consistent with conventional band-mapping results.[8] The relevant section is displayed in Fig. 1(c) with the final-state band shifted down by the amount of the photon energy.

Furthermore, some qualitative statements on the hybridization of these bands may be obtained. For example, the band 5 near Γ (the bands are numbered in the sequence of their energies at X) belongs to the representation Δ_7^2. According to the sign of the spin polarization near X it must have a Δ_7^5 character. This means it has to change its spatial symmetry from predominantly Δ_7^2 at Γ to predominantly Δ_7^5 at X. The band 3 in turn shows the reverse behavior, i.e., a change from Δ_7^5 to Δ_7^2 when going from Γ to X. Additionally the feature C has to be taken into account. Due to polarization it must be related to a transition involving a partly Δ_7^5-like initial state. These findings can be explained by a hybridization of bands 3 and 5. If one considers the band structure neglecting the spin-orbit-interaction,[9] bands of the single-group representations Δ_2 and Δ_5 are allowed to cross. In the relativistic case, however, both bands belong to the same double-group representation Δ_7, which leads to the hybridization manifesting itself in the band structure as an anticrossing around $k_\perp=0.65$. Because the bands are flat and close in energy one still observes the influence of hybridization at $k_\perp=0.85$, where the admixture of Δ_7^5 in band 3 is responsible for the occurrence of peak C. This interpretation is supported by calculations within the combined interpolation scheme,[10] by means of which we determined the relative portions of the wave functions $\{|\psi_j^i|^2\}$ transforming like the representations Δ_j^i in the occupied bands. As a result at that particular value of $k_\perp$ the ratio of these contributions in band 3 comes to $\{|\psi_7^5|^2\}/\{|\psi_7^2|^2\}=0.25/0.75$.

B. Oblique incidence of circularly polarized light

Similar experiments as described before have been carried out for the synchrotron radiation incident at an angle of $\theta_i=60°$ with respect to the surface normal. To reduce the symmetry of the complete system in a controlled way, the plane of incidence was chosen to be parallel to the $\Gamma KLUX$ mirror plane of the crystal. This geometry introduces the following effects in the photoemission process. On the one hand the degree of circularity P_c^i of the light within the crystal now depends on the angle of incidence and the photon energy and may be different from the circularity P_c^o outside, which has been determined for the 6.5m normal-incidence monochromator to be $P_c^o=90°$.[11] However, by the use of the Fresnel equations[12,13] and the optical constants of silver given by Leveque *et al.*,[14] the circularity in the case of $\theta_i=60°$ and $h\nu=12.5$ eV is estimated to be nearly the same as for $\theta_i=0°$. On the other hand, the component of the vector potential $\mathbf{A}$ perpendicular to the surface may excite transitions of the form

$$\Delta_6^1\rightarrow\Delta_6^1\quad(\mathbf{A}\|z)\ , \tag{2}$$

which are forbidden at normal incidence.

The intensity spectrum for $h\nu=12.5$ eV is displayed in Fig. 2(a) and should be compared to the corresponding one at normal incidence [Fig. 1(a)]. Both spectra are normalized to the leading peak at $E_B=-4$ eV. The relatively broad structure around $E_B=-4.5$ eV proves to be unpolarized and is therefore tentatively attributed to a transition from a high one-dimensional density of states (Δ_6^1) near Γ. The peak at $E_B=-4.3$ eV is slightly higher than at normal incidence, which also may be a contribution of a state with symmetry Δ_6^1. In the spin polarization now additionally to P_{long} [Fig. 2(b)] a component P_{trans} within the $\Gamma KLUX$ plane appears [Fig. 2(c)]. (It should be mentioned that in this case an interpretation in terms of partial intensities may fail, due to the vector character of the spin polarization.) In Fig. 3(b) the orientation of the spin-polarization vectors corresponding to the transitions at $E_B=-4$ eV (A) and $E_B=-4.3$ eV (B) is compared to the results at normal incidence [Fig. 3(a)]. The vector of

A is inclined only slightly to the surface normal, whereas in the case of B the deviation is much stronger.

A quantitative explanation for the behavior of the spin-polarization vector may be given only by one-step calculations, which take into account the optical properties of the crystal. Here we will try a qualitative approach in the frame of the three-step model, using arguments based on the symmetry of the complete system.[15]

Generally the operator O for the circularly polarized light incident along the z axis is expressed as

$$O \sim \hat{\mathbf{x}} \pm i\hat{\mathbf{y}} \; . \tag{3}$$

The wave functions in the crystal and the operator of the incident light must be referred to the same system of coordinates, which is trivial in the case of normal incidence. If the light is incident in the xz plane having an angle θ_i with respect to the surface normal, the operator keeps the form (2) only in the system of the photon (x',y',z'). i.e., $O \sim \hat{\mathbf{x}}' \pm i\hat{\mathbf{y}}'$, which after transformation into the system of the crystal becomes

$$O \sim (\hat{\mathbf{z}} \sin\theta_i - \hat{\mathbf{x}} \cos\theta_i \pm i\hat{\mathbf{y}}) \; . \tag{4}$$

This approach does not contain changes in circularity introduced by the optical properties of the metal. Now depending on the transition in question different parts of the operator (4) are effective. The transition $\Delta_7 \rightarrow \Delta_6$ is allowed for x and y polarization of the light, but forbidden for z polarization [see (1)]. Therefore only the second and third terms in (4) are effective, and the operator takes the form

$$O' \sim (-\hat{\mathbf{x}} \cos\theta_i \pm i\hat{\mathbf{y}}) \; . \tag{5}$$

Comparing this result with (3), (5) may be interpreted as an operator describing the excitation by normally incident light, which has a θ_i-dependent degree of circularity. As mentioned above, the high symmetry of the normal-incidence geometry then restricts the orientation of the spin-polarization vector to the surface normal.

If the transition is allowed also for z polarization of the incident light, which is the case for $\Delta_6 \rightarrow \Delta_6$ [$\Delta_6^5 \rightarrow \Delta_6^1$ for x and y polarization (1), $\Delta_6^1 \rightarrow \Delta_6^1$ for z polarization (2)], all terms in (4) must be considered. The loss of the yz plane

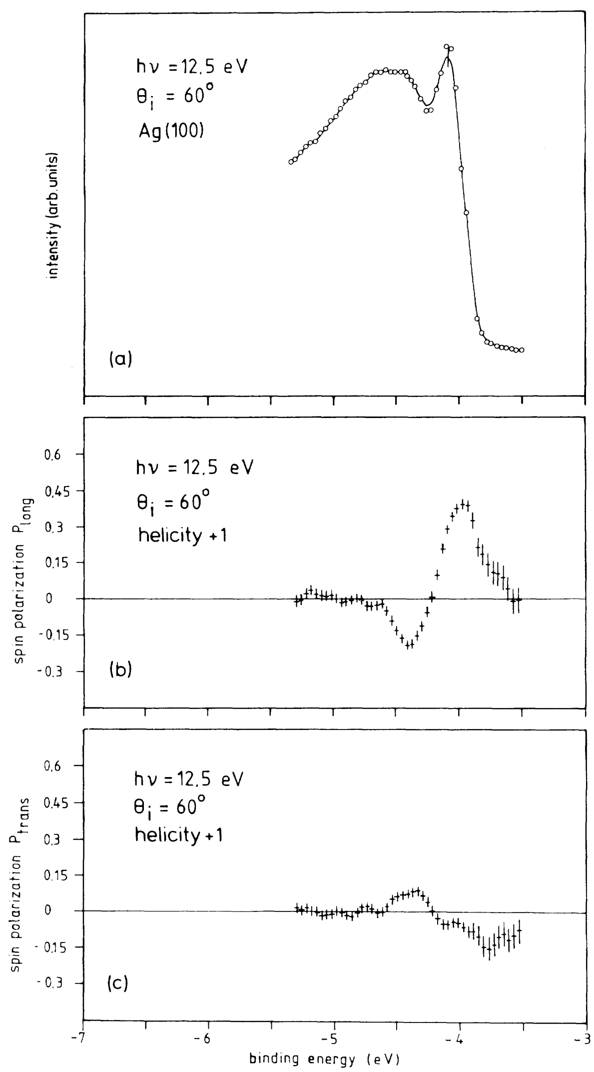

FIG. 2. (a) Energy-distribution curve of the normally emitted electrons with light incident at $\theta_i = 60°$ with respect to the surface normal. The spin polarization components (b) parallel and (c) perpendicular to the surface normal.

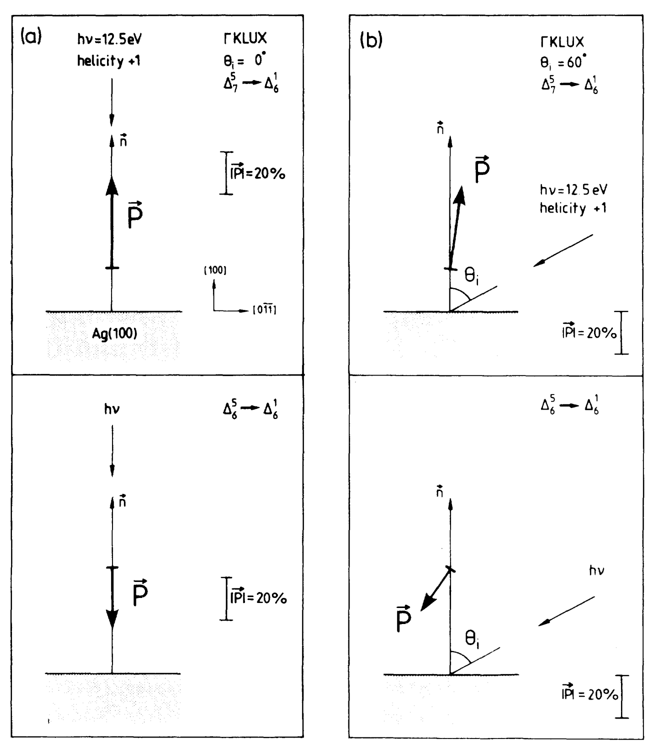

FIG. 3. Orientation of the spin-polarization vector $\mathbf{P}$ for the transitions $\Delta_7^5 \rightarrow \Delta_6^1$ ($E_B = -4$ eV) and $\Delta_6^5 \rightarrow \Delta_6^1$ ($E_B = -4.3$ eV) in the case of (a) normally incident and obliquely incident light with $\theta_i = 60°$.

as a mirror plane lowers the symmetry of the system and allows a spin-polarization vector in the *xz* plane. Due to the remaining symmetry only the component perpendicular to the *xz* plane must be zero. Therefore the hybridization of Δ_6^1 and Δ_6^1 parts in band 4 is responsible for the orientation of the spin-polarization vector. This is consistent with the results of the above-mentioned calculations, which also indicate the presence of a small contribution of Δ_6^1 in band 4. At any rate these calculations refer to the bulk band structure and do not account for the surface, whereas according to the results of one-step theories[16] this Δ_6^1-like contribution may be higher at the surface than in the bulk. As already stated, a more complete description of this effect requires the calculation of the transition matrix elements and the spin polarization using the correct wave functions obtained in the frame of a one-step theory of photoemission.

IV. CONCLUSION

We have investigated the (100) surface of silver with the method of spin- and angle-resolved photoemission using circularly polarized light. The observed spin polarization of the normally emitted electrons was consistent with the predictions from relativistic selection rules for the Δ direction. In the case of normally incident light a hybridization of the energy bands with double-group representations of Δ_7^5 and Δ_7^2 was found, the alignment of the spin-polarization vector always being parallel to the surface normal. This indicates that in this highly symmetric geometry the orientation of the spin-polarization vector is completely determined by the symmetry of the system.

If the direction of incidence was inclined to the surface normal, the orientation of the spin-polarization vector was dependent on the hybridization between Δ_6^5 and Δ_6^1 symmetries in the initial state. Thus the orientation of the spin-polarization vector may serve as a sensitive indicator for hybridizations, which involve initial states only excited by the component of the vector potential perpendicular to the surface. Similar effects should then also be observed for the Λ direction, if a hybridization of Λ_6^3 and Λ_6^1 is present, and for the Σ line.

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