Spin-orbit-induced spin polarization in W $4f$ photoemission

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The photoelectron spin polarization induced by spin-orbit interaction was studied for emission out of the W $4f$ level excited by linearly polarized light. The polarization shows a smooth variation with photon energy, in qualitative agreement with the behavior expected for a free atom, but in contrast to recent results for Cu $3p$. By determining the photon energies where the polarization vanishes the phase differences between $l+1$ and $l-1$ final-state channels are found to take on multiples of π for 75 and 275 eV, in contrast to Hartree-Fock calculations yielding 45 and 200 eV.

I. INTRODUCTION

Spin polarization of photoelectrons is caused either by exchange or by spin-orbit interaction. In ferromagnets the density of states in the valence band for spin parallel or antiparallel to the sample magnetization is different. Therefore, photoelectrons from the valence band are spin polarized. For core-level photoemission the final-state energy with core-hole spin parallel or antiparallel to the sample magnetization is different. Therefore, photoelectrons emitted from a core level are also spin polarized,[1,2] although there are equal numbers of electrons of both spin directions.

Spin-orbit interaction is the other reason for spin-polarized photoelectrons. For example, in the Fano effect[3] photoelectrons from the outer s level of alkali-metal atoms, excited with circularly polarized light, are spin polarized.[4] Strong polarization is also measured in a similar experiment by the excitation of p electrons of thallium[5,6] and lead[7] atoms with circularly polarized light. Another effect, predicted by Cherepkov[8] and Lee,[9] which is also based on spin-orbit interaction, uses linearly or unpolarized light in an angle-resolved experiment. The light incidence, the spin-polarization axis, and the electron emission direction define a handedness that is necessary for the occurrence of spin polarization. With unpolarized light spin-polarized photoelectrons have been produced from the open shell of lead atoms.[10] For photoelectrons from closed shells from xenon and argon the angular distribution of the spin polarization has been measured using linearly polarized light.[11] These experiments further show that in an angle-integrating setup the polarization vanishes.

In magnetic materials, the interplay between spin-orbit and exchange interaction is the source of magnetic dichroism. As we have shown earlier for the magnetic linear dichroism in the angular distribution[12] and for the magnetic circular dichroism,[13] it is possible to separate the two contributions if one measures the spin polarization of the photoelectrons in the dichroic spectra. If there is no magnetic order, one should still see the spin-orbit induced spin polarization. This can be checked by measuring a ferromagnet above the Curie temperature. Alternatively, the spin-orbit-induced part should also be observable in photoemission spectra of a paramagnet.

One of the motivations for our study of the spin polarization induced by spin-orbit interaction in the W $4f$ photoemission spectra comes from the results obtained for Cu $3p$.[14] There we observed a rapid variation of the spin polarization with the photon energy that was in strong contrast to the smooth photon energy dependence predicted by atomic theory.[8,14] It appears unlikely that this behavior is caused by the matrix elements and/or phases that had been used being grossly incorrect in their general photon energy dependence. Consequently, the rapid variation may be ascribed to solid-state effects, e.g., photoelectron diffraction. By investigating this effect in other materials, one may hope to be able to identify the basic physical mechanism.

II. EXPERIMENT

The experiments were performed at the U2-FSGM undulator beam line of the BESSY storage ring in Berlin[15] and the BW3/SX700 undulator beamline at HASYLAB (DESY) in Hamburg.[16] The tungsten crystal was cleaned by several flashing and oxidation cycles, and showed a sharp 1×1 low-energy electron diffraction pattern. During data acquisition the pressure in the chamber was less than 3×10^{-10} mbar. The light (s or p polarized at BESSY, p polarized at DESY) impinged onto the sample under an angle of 17° measured to the surface, as shown in Fig. 1. The electrons were collected normal to the surface with a full acceptance of (about) 8°. A commercial hemispherical analyzer equipped with the high-efficiency Fe(001) very-low-energy electron diffraction spin polarimeter[1,17] was used. The energy resolution, determined from the width of the Fermi edge, was about 500 meV. To measure the spin polarization, the magnetization of the Fe detector surface is reversed. If this magnetic-field pulse leads

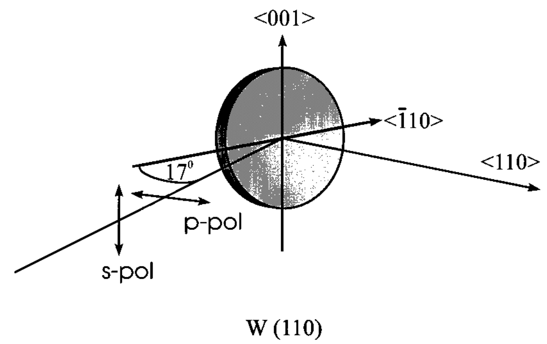

FIG. 1. Experimental geometry. The light impinges onto the tungsten surface under an angle of 17°. The electrons are collected in normal emission, i.e., parallel to the $\langle 110 \rangle$ direction. The spin polarization is measured parallel to the $\langle 001 \rangle$ direction. At the U2-FSGM beam line at BESSY both light polarizations (s and p polarized) are available, whereas the BW3 SX700 at DESY provides p-polarized light.

to remnant changes in other parts of the spectrometer, an apparatus asymmetry/spin polarization may be induced. This would also be present in parts of the spectrum where only secondary electrons contribute. In our experiment, no spin polarization in the secondaries due to an apparatus asymmetry was discernible in the region above the $4f$ peaks without any correction to the data. Consequently, apparatus asymmetry is negligible in our experiment.

At the U2-FSGM the change of the light polarization is easily possible; one only has to open the gap of the horizontal and close the gap of the vertical undulator. No further changes are necessary, which guarantees that any change in the spectra is exclusively caused by the change of the light polarization.

III. RESULTS

Figure 2 shows spin-resolved W $4f$ energy distribution curves (EDC's) obtained with a photon energy of 70 eV. With p-polarized light (upper panel) there is a strong spin polarization of the two spin-orbit split sublevels along the $\langle 001 \rangle$ direction, with different sign. With the same experimental setup, if one uses s- instead of p-polarized light, no polarization is found (EDC's in the lower panel). This shows that spin polarization occurs only for p-polarized light. Symmetry also requires that there is no polarization along the in-plane $\langle \bar{1}10 \rangle$ direction, both with s- and p-polarized light. Although this was not checked in the present experiment, it was indeed found to be the case with p-polarized light for Cu $3p$ photoemission.[14]

An example for higher photon energy is shown in Fig. 3. Here, the secondary electron background is lower. Compared to the spectra with $h\nu = 70$ eV (Fig. 2) the sign in the peaks has changed. The small flat background makes a determination of the total polarization fairly reliable. The difference (lower panel) vanishes in the region of the secondaries. The ratio of the energy integral over the difference spectrum to the integral over the absolute value of the difference spectrum is smaller than 1%. This means that the overall spin polarization vanishes within experimental error.

Usually, in soft x-ray photoelectron spectroscopy at the

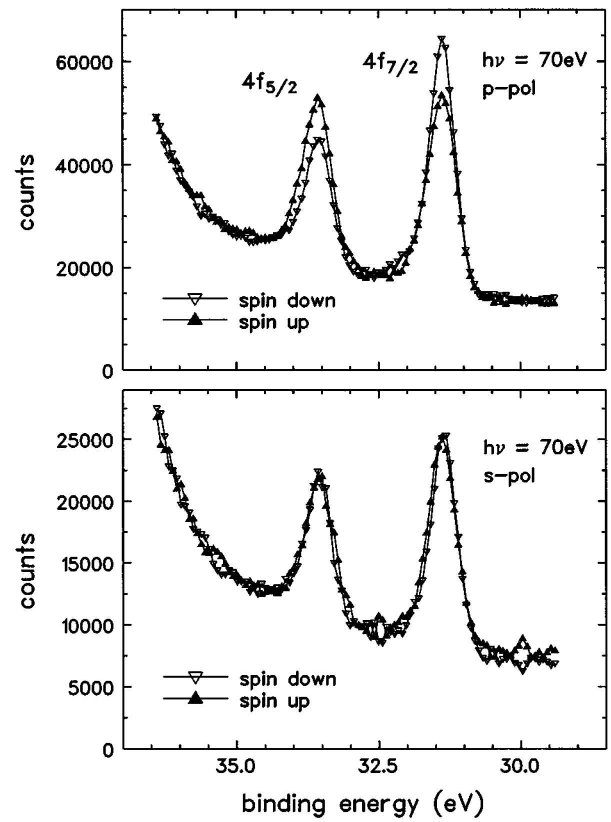

FIG. 2. Spin-resolved W $4f$ EDC's for $h\nu = 70$ eV photon energy measured with s- and p-polarized light. The open triangles mark the spin-down channel (antiparallel $\langle 001 \rangle$) and the filled triangles the spin-up channel (parallel $\langle 001 \rangle$). A strong spin polarization with different sign in the spin-orbit split sublevels is found using p-polarized light (upper panel), whereas in the same geometry but with s-polarized light no polarization occurs (lower panel).

tungsten $4f$ core-level a surface core-level shift of 0.3 eV is observable,[18] leading to a double peak (31.5 eV and 31.2 eV binding energy for W $4f_{7/2}$). Because of the energy resolution we observe only one peak at 31.4 eV with a full width at half maximum of 0.6 eV (see Fig. 3). On the other hand, oxygen on the surface also would cause a double peak, but the binding energy would be shifted 0.3 eV to higher energy and the intensity of the surface features would decrease.[18] This means that the broad peak is a superposition of the bulk and the surface contribution and no evidence for oxygen is visible.

The W $4f$ polarization was studied for several photon energies. To correct for the influence of the secondary electron background, which changes also with the photon energy, a linear background was subtracted for each peak. Then the areas of the spin-up and spin-down channels were calculated separately for each sublevel. The polarization is the ratio of the difference of the peak areas to the sum. Figure 4 shows the polarization as a function of the photon energy separately for $j = 5/2$ and $j = 7/2$ levels. The largest polarization is observed for the lowest photon energy of 60 eV. The polarization changes sign between 70 and 80 eV and reaches another maximum at 120 eV. At about 280 eV the sign changes again.

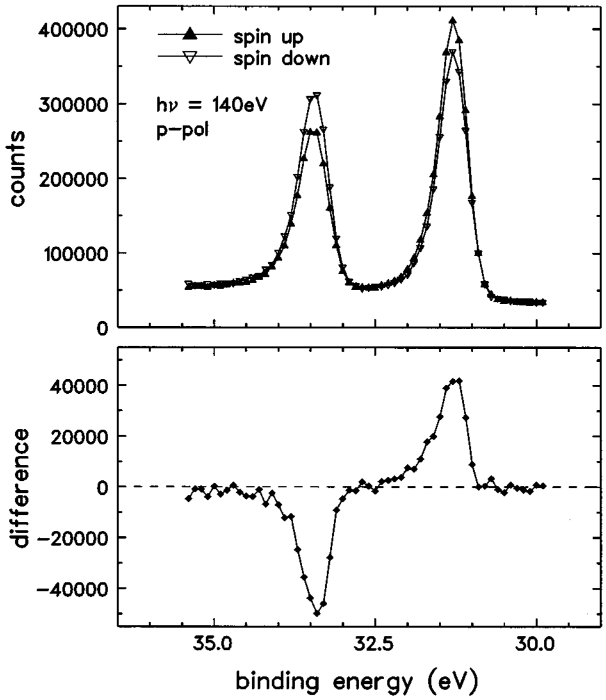

FIG. 3. Spin-resolved W 4f energy distribution curves (EDC's) measured with p-polarized light of $h\nu=140$ eV photon energy. The integral of the difference (lower panel) over the binding energy vanishes within 1% relative to the integral of the absolute value of the difference.

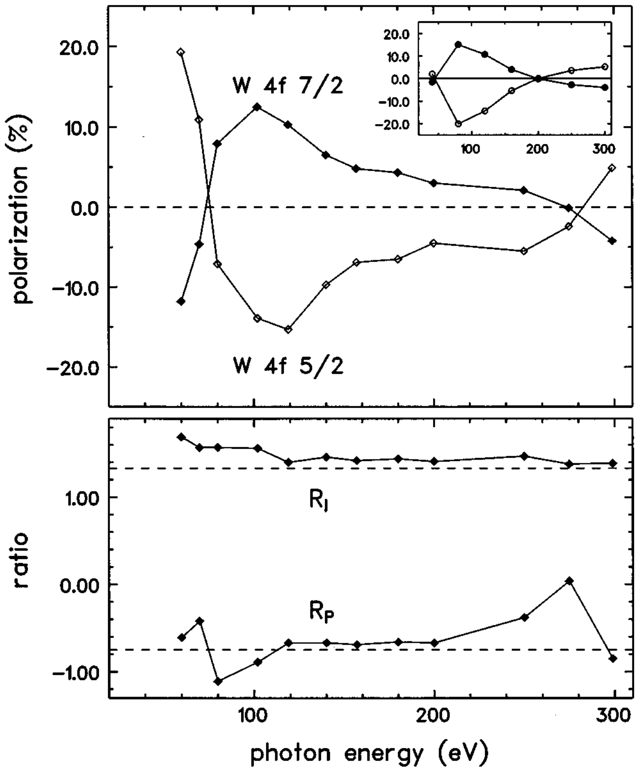

FIG. 4. Upper panel: Polarization of the spin-orbit split tungsten 4f sublevels as a function of photon energy. In the inset the calculated spin polarization for free tungsten atoms is shown (Refs. 8, 14, and 19). The lower panel shows the ratio of the $j=7/2$ to $j=5/2$ polarizations (R_P) and intensities (R_I). The dashed lines indicate the values expected within the atomic picture.

IV. DISCUSSION

As a starting point for the description of spin-resolved photoemission from a core level of a nonmagnetic atom in the lattice of a solid we use a free atom as model for the emitter. Therefore we apply the theoretical treatment for spin polarization of free atoms to our situation.[8,14] Assuming the spin-polarization axis perpendicular to the plane spanned by the light polarization vector and photoelectron momentum, the polarization for emission out of an f-core level is given by

$$P_{5/2}=6\times\frac{R_4R_2\sin(\delta_4-\delta_2)}{3R_2^2+4R_4^2}\,\frac{\sin(2\theta)}{1+0.5\beta(3\cos^2\theta-1)},\tag{4.1}$$

$$P_{7/2}=-\frac{3}{4}P_{5/2},\tag{4.2}$$

where R_4 and R_2 are the radial dipole matrix elements for g- and d-like continuum states, respectively, and $(\delta_4-\delta_2)$ is the phase difference between these final states. The angle θ is measured between the vector of the electric field and the electron emission direction; β is the asymmetry parameter. In general, the polarization of the electrons vanishes when the spin quantization axis lies in the plane defined by the light polarization vector and the electron emission direction.[8] This is experimentally confirmed for s-polarized light as shown in Fig. 2 (lower panel).

In our experiment with p-polarized light the angle θ is 17°. With tabulated values[19] for the matrix elements, the phase differences, and the asymmetry parameter we calculated the polarization of both W 4f sublevels (inset of Fig. 4). Qualitatively there is a good agreement between the experimental and theoretical results; especially, two sign changes of the polarization are reproduced. The sign of the matrix elements R_4 and R_2 is positive for all photon energies (4f levels have no Cooper minimum[19]). Therefore, all sign changes are related to the sine of the phase difference $(\delta_4-\delta_2)$. Regarding the details there are some disagreements; the polarization for low photon energies is much higher in the experiment than in the calculations, and the sign changes at different energies. Also the ratio of the polarizations of the two sublevels (R_P) deviates from the predicted value $-3/4$, especially at low and high photon energies, as shown in Table I and Fig. 4, lower panel. The product of the intensity and polarization ratio, $R_IR_P=(I_{7/2}^{\rm up}-I_{7/2}^{\rm down})/(I_{5/2}^{\rm up}-I_{5/2}^{\rm down})$, is -1 if the surplus of electrons with one spin component in the W 4$f_{7/2}$ peak is the same as the surplus of electrons with the other spin component in the W 4$f_{5/2}$ peak. In this case the overall spin polarization vanishes. Theoretically, the intensity ratio R_I is 4/3 and $R_IR_P=-1$ (see also Table I and Fig. 4, lower panel). For medium energies the ratio R_P measured in our experiment is about -0.7. Therefore, one could expect an overall polarization of the W 4f level if one takes the integral over both peaks. But this is not the case, since the experimental

TABLE I. Polarization ($R_P = P_{7/2}/P_{5/2}$) and integrated intensity ($R_I = I_{7/2}/I_{5/2}$) (branching) ratios of the W $4f_{7/2}$ and W $4f_{5/2}$ sublevels as functions of the photon energy. In the integral over both peaks the polarization should vanish within the theoretical treatment for free atoms (values in the first column); therefore the product of both values ($R_P R_I$) must be -1.

$h\nu$ (eV)	theor.	60	70	80	102	119	140	157	180	200	250	275	299
R_P	−0.75	−0.61	−0.42	−1.11	−0.89	−0.67	−0.67	−0.69	−0.66	−0.67	−0.38	0.04	−0.85
R_I	1.33	1.69	1.57	1.57	1.56	1.40	1.46	1.42	1.44	1.41	1.47	1.38	1.39
$R_P R_I$	−1	−1.03	−0.66	−1.73	−1.39	−0.94	−0.97	−0.99	−0.96	−0.94	−0.56	0.05	−1.20

intensity ratio also deviates from the theoretical value (see Table I and Fig. 4). Only for low ($h\nu = 70$ eV, 80 eV, and 102 eV) and high ($h\nu = 250$ eV and 275 eV) photon energies the ratios of the polarizations and intensities yield an overall polarization (i.e., the energy integral over the polarization of both sublevels has a nonzero value). In our experimental setup spin-dependent transmission through the surface, as reported by Refs. 20 and 21, does not matter since we measured in normal emission.

The photon energy dependence is in qualitative agreement with the behavior expected for the free atom. This is in contrast to the rapid variation found for Cu $3p$.[14] At present this rapid variation observed on Cu is not understood. Presumably, photoelectron diffraction (PED) is the cause. The qualitatively different energy dependence found here may be due to a number of reasons. The main difference is the different angular momentum character of the core level investigated, and, consequently, also that of the final states. For emission out of an f level, final states of d and g character are accessible. It is known that photoelectron diffraction, especially at low kinetic energies, depends strongly on the angular momentum character of the final state.[23–26] To elucidate this point further, angular dependences of the spin polarization,[22] as well as other materials, are being studied.

V. CONCLUSION

Photoelectrons emitted from the tungsten $4f$ core levels are spin polarized along the quantization axis normal to the reaction plane if p-polarized light is used, whereas s-polarized light causes no spin polarization. This agrees with the theoretical description for free atoms. The polarization as a function of photon energy ($h\nu = 60-300$ eV) changes sign two times. This is also predicted by the formulas for the free atom, although the exact zero crossing energy is different in experiment and theory. For medium photon energies the calculated and measured polarizations agree well, and also the products of the intensity and polarization ratios are close to -1 as expected from the theory. Discrepancies between experiment and theory appear for high and low photon energies; at $h\nu = 60$ eV the measured polarization is much higher than calculated.

One may use the W $4f$ level as an internal source of spin-polarized electrons in studies of ultrathin magnetic structures, e.g., Fe has been investigated extensively. If a magnetic film is deposited on a W surface, and excitation is such that the W $4f$ spin-orbit-induced polarization is collinear with the magnetization in the film, then a possible spin dependence of the electron transmission through the magnetic film will affect the intensities of the $4f$ photoemission lines. Such an experiment should be done away from the zero crossing of the polarization, since there the polarization is small, and the ratio between 5/2 and 7/2 polarization deviates from the statistical one. For photon energies around 120 eV one has a sizable spin polarization, and by comparing a possible effect for the 5/2 and 7/2 level, one has an internal standard.

Since the polarization shows a smooth photon energy dependence, it is apparently not affected strongly by photoelectron diffraction. In particular, the photon energies at which the polarization vanishes can be identified, with the phase difference assuming a multiple of π. This occurs for 75 and 275 eV, compared to the theoretical 45 and 200 eV. This deviation may be due to approximations used in the calculation of the phase difference, which have been calculated in Hartree-Fock with a charge density $\rho(r)$ appropriate to a free atom.[19] Presumably, the phase difference is influenced by the detailed shape of the atomic potential at relatively far distances from the nucleus. Therefore, experiments such as these may provide a check for different models.

Spin-orbit-induced spin polarization should also be observable under excitation with circularly polarized light. Since in that case the polarization (measured parallel to light helicity) is not primarily an interference effect, there should be a polarization at energies where the polarization vanishes for linearly polarized light due to the phase difference. By comparing data for both polarizations one may determine the matrix elements for both final-state channels. This is an alternative to the study of the angular dependence as performed, e.g., on gas phase samples, which is not useful for solids because of PED. In this way one may completely characterize the excitation process.

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