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Zürcher, P.; Meier, F.; Christensen, N. E.

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Optically Polarized Conduction-Band Electrons in Tungsten Observed by Spin-Polarized Photoemission

P. Zürcher and F. Meier

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

and

N. E. Christensen

Physics Laboratory I, The Technical University of Denmark, Copenhagen DK-2800, Denmark

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Along the (100) direction of tungsten, interband transitions induced by circularly polarized light of energy $1.5 \text{ eV} \leq h\nu \leq 4.1 \text{ eV}$ lead to spin polarization of the excited conduction electrons. This is observed by measuring the spin polarization of the photoelectrons emitted from a cesiated crystal surface. The measured polarization values depend sensitively on the s -, p -, and d -hybridization properties of the conduction bands. Excited-state lifetimes are obtained from the widths of the polarization structures.

The now widespread use of synchrotron radiation in angular resolved photoemission has made it increasingly clear that the optical selection rules for linearly polarized light provide an elegant means for identifying the parity of electronic states.¹ In this paper we show that the symmetry properties of the electronic wave functions can be investigated in further detail by photoemission using circularly polarized light. The present technique requires the measurement of the spin polarization of the photoelectrons.

The experiment is based on the fact that unpolarized electrons can be excited by circularly polarized light into spin-polarized final states. Although such optical polarization experiments have been made earlier with use of selected transitions in semiconductors,^{2,3} only the present measurements with tungsten indicate that final-state polarization can be obtained under very general conditions also for metals.⁴ Therefore it appears worthwhile to explore the possibilities of this method systematically. As it relies on the selection rules for circularly polarized light, the symmetry of the electronic states is of crucial importance. A decomposition into spin orbitals of

given l value (l is the orbital angular momentum quantum number) is useful. The symmetry properties of the spin orbitals are found from group theory. The spin polarization in each excited state is determined by the mixing of the spin-"up" and -"down" components in this state.

Essential points of the experiment are as follows: (i) The axial vector defining the direction of the final-state spin polarization is given by the spin direction of the circularly polarized light. (ii) In the absence of spin-orbit coupling the electronic wave functions are pure spin states. Then, because light interacts only with the orbital motion of the electrons, spin-up and -down electrons participate identically in all transitions and no overall spin polarization is obtained. Therefore spin mixing by spin-orbit interaction in at least one of the states involved in a given transition is necessary for final-state spin polarization. (iii) Simple symmetry considerations show that for crystals with inversion symmetry, as, e.g., tungsten, transitions produced by right- and left-circularly polarized light have the same absolute values of the polarization but opposite signs.

Tungsten was chosen for this experiment because it shows appreciable spin-orbit interaction,⁵ is readily available as single crystals,⁶ is easy to clean, and has a band structure that is quite well known.⁵ Our specimen was a W(100) single-crystal platelet of 5 mm diam. It was cleaned by up to twenty successive cycles consisting of heat treatment at 1800°C (duration 30 sec) followed by exposure to 5×10^{-6} Torr of oxygen during 2.5 min at 1600°C. As final step, after the last oxygen exposure, the carbon monoxide and sulfur oxide were evaporated by flash heating to 2100°C. The surface condition was checked by low-energy-electron-diffraction (LEED)-Auger analysis. The LEED pattern was identical to the one reported by Melmed, Layer, and Kruger⁷ for a clean W(100) surface. Traces of sulfur could still be detected in the Auger signal, whereas the carbon signal was very weak and no indication of oxygen could be found. In order to investigate the band structure at low energies, $h\nu < 5$ eV, the crystals were cesiated to reduce the work function. A detailed account of the experimental setup to measure the spin polarization has been given before.⁸ The measurements were done at a pressure of 4×10^{-10} Torr with the sample held at a temperature of -40°C .

The polarization spectra for two samples with work function $\Phi = 1.5$ eV and $\Phi = 2.4$ eV are shown in Fig. 1. At photon energies $h\nu = 2.1$ eV and $h\nu = 2.9$ eV maxima of the polarization, -6% and $+7.5\%$, respectively, are observed for the low-work-function sample. These transitions are denoted by T_1 and T_2 . A comparison of the two spectra shows that both are identical in the common range of photon energies.

A theoretical prediction of the polarization spectrum has been published by Reyes and Helman.⁹ From group theory the symmetry of the s - p - and d -derived conduction-band states is determined along the normal to the W(100) face, i.e., the Δ direction. Then the allowed optical transitions are found by applying the selection rules for circularly polarized light. The predicted high polarizations (-100% for T_1 , $+100\%$ for T_2) could not be observed. There is a sign reversal of the polarization at $h\nu = 2.4$ eV in qualitative agreement with Ref. 9 but it occurs at a photon energy 0.4 eV higher than predicted. The crossing point of the polarization spectra with the $P = 0$ line was reproducible within 60 meV in six experiments.

The discussion of these discrepancies must take into account that the theory was developed exclusively for transitions along Δ , whereas in

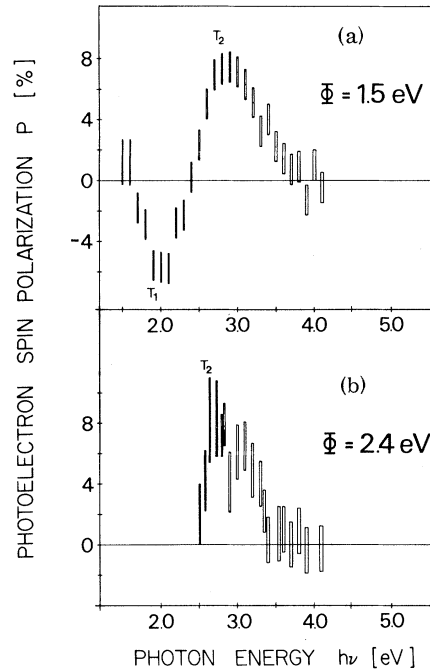


FIG. 1. W(100) single-crystal surface: Dependence of the photoelectron spin polarization P on photon energy for two cesiated samples with work functions (a) $\Phi = 1.5$ eV and (b) $\Phi = 2.4$ eV.

the experiment the acceptance angle was not externally restricted. We observe, however, that in the present case the escape cone does not influence the absolute value of the spin polarization. The spectra of the two samples with different work functions and hence with different escape cones (Fig. 1) look, indeed, very similar in the common $h\nu$ range. This is consistent with the calculated band structure of tungsten⁵ which shows that the escape cone for the T_1 and T_2 transitions is less than $\pm 14^\circ$.

From Fig. 1 we deduce that T_1 and T_2 are due to direct transitions since T_1 is simply cut off when the work function is increased from 1.5 to 2.4 eV. This is a further proof that direct bulk transitions occur in tungsten.¹⁰ It also makes clear that the T_2 structure is not due to transitions near Γ ($\Delta_{6,7} \rightarrow \Delta_7$) because T_2 should then also vanish upon increasing the vacuum level to 2.4 eV.

The only effect which we attribute to the escape cone is that the measured maxima of the polarization occur at energies 0.3–0.5 eV higher than expected from Fig. 2. The shape of the energy surfaces near the Δ direction and the corresponding partial joint density of states (PJDOS) (see

Fig. 3) cause the maximum transition probability to occur at light energies slightly higher than those needed for transitions on the Δ line. This also explains the position of the zero crossing in Fig. 1(a) to within ~ 0.2 eV, which is probably about the accuracy of the band-structure calculation.

Although the transitions responsible for the polarization structure can be unambiguously identified in Fig. 2, the interpretation of the degree of polarization produced by these transitions is a more difficult problem. Depolarization of the photoelectrons by spin-exchange scattering with the cesium on the surface is negligible. The sample with $\Phi = 2.4$ eV is less cesiated than the one with $\Phi = 1.5$ eV. Nevertheless the polarization of the T_2 transition is the same in both cases. This is not surprising because only 0.25 of a cesium monolayer is necessary to obtain $\Phi = 1.5$ eV.¹¹ At these low coverages the cesium is ionized and has a rare-gas electron configuration with zero spin. Also measurements with slightly cesiated nickel and GaAs never gave a clear indication for depolarization.^{2, 12}

In addition to the bulk interband transitions T_1

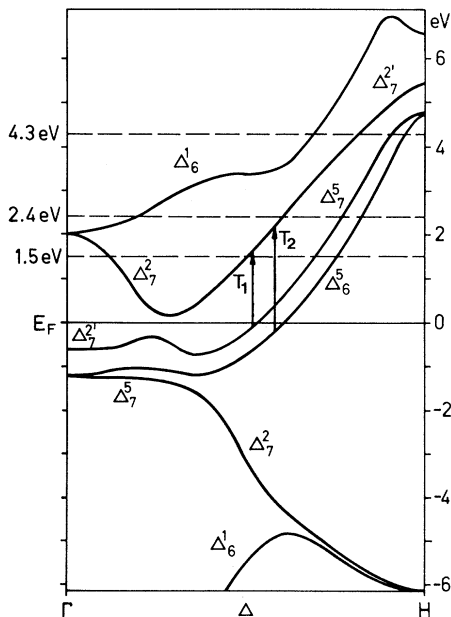


FIG. 2. Electronic energy-band structure of tungsten for the (100) direction according to Ref. 5. The vacuum levels for the free surface (4.3 eV) and the two cesiated surfaces (2.4 and 1.5 eV) are indicated. Because of the curvature of the energy bands near Γ -H, the finite escape cone, and the lifetime broadening, the T_2 transition is also observed for the 2.4-eV photothreshold.

and T_2 there are photoelectrons produced by direct emission usually referred to as surface photoemission. In the present experiment this surface emission is unpolarized as can be seen from Fig. 1. For instance, the $\phi = 1.5$ eV sample shows surface emission near threshold because no emitting interband transitions are possible at this energy; see Fig. 3.

Also at light energies above threshold the spectra of Fig. 1 give no indication of polarized surface emission. As a continuum of final states is available in surface emission any polarization structure would depend on $h\nu - \phi$ alone and not on the details of the band structure. However, the spectra shown in Fig. 1 are unambiguously due to bulk interband transitions. In particular, the polarization peak T_2 occurs at a well-defined light energy independent of the value of the photothreshold.

Also at higher photon energies surface emission makes a large contribution to the total photocurrent. For the three high-symmetry surfaces of tungsten the interband transitions at $h\nu = 10.2$ eV are superposed on a background of surface emission which amounts to 70–85% of the total photocurrent.¹⁰ The surface emission is proportional to the surface density of states which is well known for tungsten.¹⁰ The PJDOS giving rise to T_1 and T_2 shown in Fig. 3 takes into account the acceptance angle of the apparatus and the requirements that the initial state be below the Fermi level and the final state above the vacuum level. Figure 3 shows that the PJDOS of T_1 and T_2 is quite insensitive as to whether the acceptance

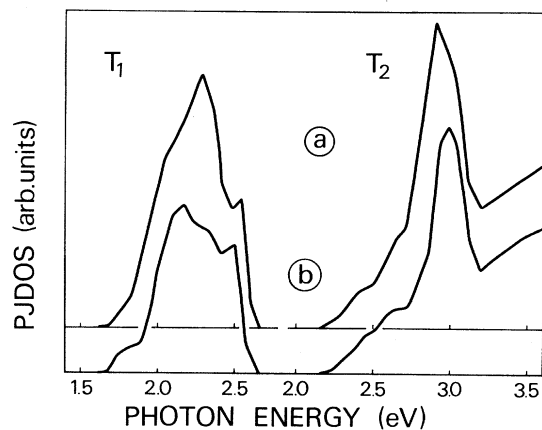


FIG. 3. Partial joint density-of-states (PJDOS) functions of W(100) for the transitions T_1 and T_2 in a sample with work function 1.5 eV, for an acceptance angle of (a) $\pm 90^\circ$, (b) $\pm 45^\circ$.

angle is $\pm 45^\circ$ or $\pm 90^\circ$. Therefore the ratio of surface to total (= surface + bulk) emission can be estimated for cesiated tungsten at photon energies corresponding to T_1 and T_2 . Average values of this ratio are taken over the widths of the transitions T_1 and T_2 . For $1.7 \text{ eV} \leq h\nu \leq 2.2$ and $2.3 \text{ eV} \leq h\nu \leq 3.2 \text{ eV}$ they are found to be $(49 \pm 5)\%$ and $(75 \pm 4)\%$, respectively. Allowing for this unpolarized surface emission and the small overlap of T_1 and T_2 due to lifetime broadening, the initial polarizations P_1 and P_2 of T_1 and T_2 are estimated to be $(-16 \pm 6)\%$ and $(32 \pm 10)\%$, respectively. This is still far off the theoretically predicted $\pm 100\%$. In Ref. 9 the final-state Δ_7 band of the T_1 and T_2 transitions is assumed to be purely d type. This is questionable since strong hybridization with p -type functions of proper symmetry is expected near the band-crossing region. We then conclude that it is this hybridization which reduces the polarization drastically. The \vec{k} -dependent hybridization of the $\Delta_7^{2'}$ and $\Delta_7^{2'}$ wave functions in the final state of T_1 and T_2 and in the initial state of T_1 is estimated from the relation

$$a = 2P^{-1}[P + 1 - (1 - P^2)^{1/2}],$$

where a and $(1 - a)$ are the $\Delta_7^{2'}$ and Δ_7^5 contributions to the final-state wave functions, respectively: With the initial polarizations P_1 and P_2 one obtains the following results: For \vec{k} values corresponding to the T_1 transition the final state is $(54 \pm 2)\%$ d type of $\Delta_7^{2'}$ symmetry and $(46 \pm 2)\%$ p and d type of Δ_7^5 symmetry. At larger \vec{k} values belonging to the T_2 transition the corresponding values are $(58.5 \pm 2.5)\%$ and $(41.5 \pm 2.5)\%$, respectively.

For the Δ_7^5 initial states the d and pd contributions are interchanged, whereas for the Δ_6^5 initial states it is not possible to obtain the hybridization from the electron-spin-polarization results presented in this Letter. With regard to these hybridized states, the change of sign of the polarization of the T_1 and T_2 transitions is due to the double degeneration of the states by time-reversal symmetry. Whereas one of these states is excited by T_1 , it is the time-reversed state with the other sign of polarization which is excited by T_2 .

The widths of the measured polarization peaks T_1 and T_2 can be used to determine the lifetime of the excited states. This method supplements one based on energy distribution curves¹³ but requires the measurement of only one spectrum. In order to avoid effects due to overlapping tran-

sitions only the low-energy side of the peaks is used to determine the full width at half maximum, Γ . For T_1 we obtain $\Gamma = 0.35 \pm 0.09 \text{ eV}$ and for T_2 the value is $\Gamma = 0.52 \pm 0.10 \text{ eV}$. The error margins are derived from the estimated uncertainty of the calculated surface emission, the uncertainty of the widths of the measured polarization peaks, and the statistical errors of the measured polarization values. The corresponding lifetimes are $(2.0 \pm 0.5) \times 10^{-15} \text{ sec}$ and $(1.3 \pm 0.25) \times 10^{-15} \text{ sec}$. From knowledge of the group velocity of the excited electrons⁵ the escape depths $l(E)$, where E is the final-state energy above the Fermi level, are obtained. For the T_1 transition ($E = 1.95 \text{ eV}$) it is $14 \pm 4 \text{ \AA}$ and for the T_2 transition ($E = 2.35 \text{ eV}$), $9 \pm 2 \text{ \AA}$. These values fill a sparsely documented part of the well-known universal $l(E)$ curve.¹⁴

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