# Supplemental material 

Spin polarization and attosecond time delay in photoemission from spin degenerate states of solids

Mauro Fanciulli ${ }^{1,2}$, Henrieta Volfová ${ }^{3}$, Stefan Muff ${ }^{1,2}$, Jürgen Braun ${ }^{3}$, Hubert Ebert ${ }^{3}$, Jan Minár ${ }^{3,4}$, Ulrich Heinzmann ${ }^{5}$, J. Hugo Dil ${ }^{1,2}$<br>${ }^{1}$ Institut de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland<br>${ }^{2}$ Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland<br>${ }^{3}$ Department of Chemistry, Ludwig Maximillian University, D-81377 Munich, Germany<br>${ }^{4}$ New Technologies-Research Center, University of West Bohemia, CZ-30614 Pilsen, Czech Republic<br>${ }^{5}$ Faculty of Physics, University of Bielefeld, D-33501 Bielefeld, Germany

(Dated: January 10, 2017)

## CONTENTS

I. Details of the model ..... 2
I.A. Geometrical corrections ..... 2
I.B. Estimate of the time delay ..... 3
I.C. Lower and upper limits for $\left|\tau_{\text {EwS }}\right|$ : a better estimate ..... 3
I.D. Influence of $\dot{r} \neq 0$ on the estimate of $\left|\tau_{\text {EwS }}\right|$ ..... 4
I.E. Spurious effects ..... 5
II. Additional measurements ..... 6
II.A. Rashba splitting of the surface state ..... 6
II.B. Comparison with $\mathrm{Au}(111)$ ..... 6
II.C. Spin-resolved EDCs of the $3 p$ core levels ..... 7
III. Comment in relation to the Heisenberg's uncertainty principle ..... 8
References ..... 8

## I. DETAILS OF THE MODEL

## I.A. Geometrical corrections

As described in Eq. (2) of the main text, the expression for the spin polarization vector $\boldsymbol{P}$ contains a geometrical correction factor $f(\boldsymbol{\Omega})$, where $\boldsymbol{\Omega}$ is the set of the relevant angles describing the symmetry of the system.

In the case of atomic photoionization, by symmetry arguments it can be shown ${ }^{14}$ that the direction $\hat{\boldsymbol{n}}$ of the vector $\boldsymbol{P}$ has to be perpendicular to the reaction plane defined by the light electric field $\boldsymbol{E}$ and the electron momentum $\boldsymbol{k}$. In the sample coordinate frame of the experimental setup described in Fig. 1 (b) of the main text, this direction corresponds to $y$. From this consideration it follows ${ }^{14}$ that the angle $\gamma$ between $\boldsymbol{E}$ and $\boldsymbol{k}$ is the only relevant one and that the correction factor is $f(\boldsymbol{\Omega})=f(\gamma)=4 \sin \gamma \cos \gamma$.

When the symmetry is reduced as in solid state targets, the reaction plane perpendicular to $\boldsymbol{P}$ is not necessarily the same, and the relevant angles become $\boldsymbol{\Omega}=(\gamma, \theta, \psi, \delta)$. The angle $\theta$ is the angle scanned during the experiment in order to perform an MDC and thus access the electronic band with momentum resolution, as it was described in Fig. 1(b) of the main text, and it is shown in Fig. I(a) together with the angles $\gamma, \chi=(\gamma-\theta)$ and $\alpha=(\gamma / 2-\theta)$. The angles $\psi$ and $\delta$ are the elevation angles of $\boldsymbol{P}$ from the $x y$ and $y z$ planes, respectively, as shown in Fig. I(b), and thus are always between $0^{\circ}$ and $90^{\circ}$. The angles $\chi$ and $\theta$ can be used to evaluate the ratios $E_{x} / E_{z}=\tan \chi$ and $k_{x} / k_{z}=\tan \theta$.


FIG. I. Definition of the relevant symmetry angles: (a) $\gamma, \theta, \alpha, \chi$; (b) $\psi, \delta$.

The geometrical correction factor has still the form $f=4 \sin \gamma^{\prime} \cos \gamma^{\prime}$, where now $\gamma^{\prime}=\gamma^{\prime}(\gamma, \alpha, \psi, \delta)$ is the equivalent angle in the new reaction plane (i.e. the angle between the projections of $\boldsymbol{E}$ and $\boldsymbol{k}$ in the plane perpendicular to the spin polarization vector). By use of the parametric Weierstrass substitution $t \doteq \tan \left(\gamma^{\prime} / 2\right)$, one can evaluate:

$$
\begin{equation*}
f(\boldsymbol{\Omega})=4 \sin \gamma^{\prime} \cos \gamma^{\prime}=8 t \frac{1-t^{2}}{\left(1+t^{2}\right)^{2}} \tag{S1}
\end{equation*}
$$

and the parameter $t\left(\gamma^{\prime}(\gamma, \alpha, \psi, \delta)\right)$ is calculated with trigonometry construction as:

$$
\begin{equation*}
t \doteq \tan \left(\frac{\gamma^{\prime}}{2}\right)=\tan \left(\frac{\gamma}{2}\right)\left(\frac{\cos \psi}{\cos \delta} \cos ^{2} \alpha+\frac{\cos \delta}{\cos \psi} \sin ^{2} \alpha\right) \tag{S2}
\end{equation*}
$$

In the experimental setup of the COPHEE endstation described in Fig. 1 (b) the angle $\gamma$ is fixed at $\gamma=\pi / 4$. For the measurement performed at $h \nu=130 \mathrm{eV}, \theta$ is varied between $9.5^{\circ}$ and $12.5^{\circ}$, and $\delta$ and $\psi$ are measured as $\delta=0^{\circ}$ and $\psi=51^{\circ}$. These measured values are the average of the different $E_{b}$ measurements, since they all are within a range of $\pm 5^{\circ}$, which correspond to the experimental capabilities of the setup. Given the small variation of $\theta$ one can easily check that the variation of the correction factor $f$ when scanning the band is negligible. By using $\theta=11^{\circ}$ one obtains $t=0.28$ and $f=1.76$. For completeness, by using the several measured values of $\delta$ and $\psi$ for the different $E_{b}$ we obtain the two ranges $t \in[0.25,0.30]$ and $f \in[1.65,1.84]$. It has to be pointed out that for the atomic case one would simply have $\gamma^{\prime}=\gamma=\pi / 4$ and thus $t=0.41$ and $f=2$.

It is important to note that in order to explain the deviation of the reaction plane from the atomic case, the crystal planes as shown in Fig. I and the orbital symmetries should be taken explicitly into account.

## I.B. Estimate of the time delay

As discussed in the main text, an estimate of $\tau_{\text {EWS }}$ can be obtained from eq. (4) with the approximation $\dot{r} \approx 0$. The simplified equation becomes:

$$
\begin{equation*}
\tau_{\mathrm{EWS}} \approx \frac{-\hbar \dot{P}}{\partial P / \partial \phi} \tag{S3}
\end{equation*}
$$

The signs of $\dot{P}$ and $\partial P / \partial \phi$ determine the sign of $\tau_{\text {EWS }}$. This in general can be positive or negative, meaning a delay or an advance of one interfering transition with respect to the other. However our experiment is not sensitive to the actual sign, since without any further developments on the orientation in space of the spin polarization vector with respect to the actual transitions involved the sign of the measured $\boldsymbol{P}$ does not give any information. This is why in eq. (5) absolute values are considered.

Without any assumption on the actual values of $r$ and $\phi$ themselves, we can obtain from eq. (S3) the estimate for $\left|\tau_{\text {Ews }}\right|$ as shown in eq. (5) of the main text, where one needs to evaluate the coefficient $c=\hbar / \max |\partial P / \partial \phi|$. In order to do this, by using $I_{t o t}=2 \sin ^{2} \gamma^{\prime} R_{1}^{2}+2 \cos ^{2} \gamma^{\prime} R_{2}^{2}$ (see refs. ${ }^{25,26}$ ), where $R_{1,2}$ are the radial part of the matrix elements describing the transitions $T_{1,2}$, the eq. (2) of the main text can be explicitly rewritten as:

$$
\begin{equation*}
P=\frac{2 \tan \gamma^{\prime} r}{\tan ^{2} \gamma^{\prime}+r^{2}} \sin \phi=\frac{4 t\left(1-t^{2}\right) r}{4 t^{2}+r^{2}\left(1-t^{2}\right)^{2}} \sin \phi \tag{S4}
\end{equation*}
$$

where the coefficient $t$ has been introduced in Section IA. As a first estimate, it can be verified that $\forall t, \max |\partial P / \partial \phi| \leq 1$ (the maximum $|\partial P / \partial \phi|=1$ occurs for $\phi=\kappa \pi$, with $\kappa$ integer, and in particular with the measured value $t=0.28$ it occurs for $r=0.61$ ). Therefore one obtains $c=\hbar \approx 658 \mathrm{as} \cdot \mathrm{eV}$, which enters eq. (5) of the main text and brings to the estimate $\left|\tau_{\text {EwS }}\right|>26$ as from the measured value $\dot{P}=0.04 \mathrm{eV}^{-1}$.

It has to be noticed that this estimate does not require any assumption on the actual values of $r$ and $\phi$ themselves. Also, the precise value of $t$ which comes from the measured direction of the spin polarization vector does not enter in this estimate of an inferior limit for $\left|\tau_{\text {Ews }}\right|$. In Fig. II the general dependence of $\left|\tau_{\text {EwS }}\right|$ on $r$ and $\phi$ is shown, obtained by combining eq. (S3) with eq. (S4), where $t=0.28$.


FIG. II. Dependence of $\left|\tau_{\text {Ews }}\right|$ on $r$ and $\phi$. The phase is varied between $|\phi|=[0, \pi / 2)$ in steps of $\pi / 32$. The inset shows a zoom of a 130 as time scale.

## I.C. Lower and upper limits for $\left|\tau_{\text {ews }}\right|$ : a better estimate

In this section we still consider the approximation $\dot{r} \approx 0$ to be valid. The estimate of $\left|\tau_{\text {EwS }}\right|$ can be improved by observing that $r$ is bounded by eq. (S4) for a given measured value of spin polarization. For $P=[0.09,0.2]$ from Fig. 2(e) of the main text, solving the inequality:

$$
\begin{equation*}
\left|\frac{4 t^{2}+r^{2}\left(1-t^{2}\right)^{2}}{4 t\left(1-t^{2}\right) r} P\right|=|\sin \phi| \leq 1 \tag{S5}
\end{equation*}
$$

for $t=0.28$ from Section IA one obtains $r \in[0.03,13.47]$ and $r \in[0.07,6.01]$ for the two extremes $P=0.09$ and $P=0.2$, respectively. Since $\dot{r} \approx 0$, we can consider only the second smaller range.

We can also obtain the range of allowed values of $\phi$ by using eq. (S4) and the corresponding value of $P$ for each $E_{b}$, as shown in Fig. III. In this way we can determine that $\phi \in[0.09,1.53]$.


FIG. III. Dependence of $\phi$ on $r$ and $P$. The spin polarization is varied between the extreme measured values 0.09 and 0.2 .

Therefore we can evaluate the lower and upper limits of $\left|\tau_{\text {EWS }}\right|$ that occur for $(r, \phi)=(0.61,0.09)$ and $(r, \phi)=$ $(6.01,1.53)$ respectively. This brings to the estimate 26 as $<\left|\tau_{\text {Ews }}\right|<3224 \mathrm{as}$, and its dependence on $(r, \phi)$ is summarized in Fig. IV. However it is worth to notice that the upper limit is strongly reduced as soon as the parameters $(r, \phi)$ do not assume values close to their extremes, which are very unlikely to occur in the interference process. For example, if we restrict ourselves to the realistic ranges $r \in[0.3,3]$ and $\phi \in[0.09,1]$ (since $t$ and $r$ are considered constant, if $P$ varies by a factor of 2 also $\phi$ should only vary by about 2 according to eq. (S4)), then the upper limit becomes only 125 as.


FIG. IV. Dependence of $\left|\tau_{\text {EWS }}\right|$ on $\phi$ and $r$. (a) The phase is varied between $|\phi|=[0.09,1.53]$ in steps of 0.02 ; (b) the ratio $r$ is varied between $|r|=[0.07,6.01]$ in steps of 0.3 . The insets show a zoom of a 130 as time scale.

## I.D. Influence of $\dot{r} \neq 0$ on the estimate of $\left|\tau_{\text {ews }}\right|$

We now consider the case when the approximation $\dot{r} \approx 0$ is not valid, and the simplest case to consider is to assume a linear variation with $E_{b}$. The maximum allowed value for the reasons discussed previously would be: $\dot{r}_{\max }=(13.47-0.03) /(1.8 \mathrm{eV}) \approx 7.5 \mathrm{eV}^{-1}$. By using the eq. (4) of the main text and by evaluating the two partial derivatives of $P$ with respect to $r$ and $\phi$ from eq. (S4) we can obtain the new expression of $\left|\tau_{\text {Ews }}\right|$, which is plotted in Fig. V. Noticeably, in this case there are values for which the time-delay is zero, which means that the variation with $E_{b}$ of the spin polarization is entirely due to variation of radial part of the matrix elements. The most general and most reasonable scenario has to consider variations in both phase shifts (i.e. $\left|\tau_{\text {EwS }}\right| \neq 0$ ) and radial parts.


FIG. V. Dependence of $\left|\tau_{\text {Ews }}\right|$ on $r$ and $\phi$ when $\dot{r}=7.5 \neq 0$. The phase is varied between $|\phi|=[0.09,1.53]$ by steps of 0.02 . The inset shows a zoom of a 510 as time scale.

At this stage, however, we would like to underline that we see no evidence in our data for a significant change in $r$ and that the main message of this work is the measurement of a finite $\dot{P}$ which is related to a finite $\left|\tau_{\text {Ews }}\right|$. A better theoretical model for $P(r, \phi)$ in spin-degenerate dispersive bands of a solid and better experimental setups could bring to a more precise estimation of the time-delay.

## I.E. Spurious effects

In the case of photoemission from crystals there might be other spurious effects that contribute to a spin polarization signal with respect to the simpler case of atomic targets. Such effects, related to diffraction through the surface for instance, will affect the measured spin polarization $\boldsymbol{P}_{\boldsymbol{m}}$ with an additional term: $\boldsymbol{P}_{\boldsymbol{m}}=\boldsymbol{P}+\boldsymbol{\eta}$. In general, this effects could even change the direction of $\boldsymbol{P}_{\boldsymbol{m}}$ away from $\hat{\boldsymbol{n}}$. Also, eq. (3) becomes:

$$
\begin{equation*}
\tau_{\mathrm{EWS}}=\frac{-\hbar}{\partial P / \partial \phi}\left(\dot{P}_{n}-\dot{r} \partial P / \partial r-\dot{\eta}_{n}\right) \tag{S6}
\end{equation*}
$$

where we indicated with $P_{n}$ and $\eta_{n}$ the components of $\boldsymbol{P}_{\boldsymbol{m}}$ and $\boldsymbol{\eta}$ along $\hat{\boldsymbol{n}}$. The survey of spin resolved EDCs over the $3 p$ core levels of $\mathrm{Cu}(111)$ discussed in Section II.C, however, shows that in our case diffraction effects are not relevant since the measured spin polarization is the same under different angles.

## II. ADDITIONAL MEASUREMENTS

## II.A. Rashba splitting of the surface state

The measured $\mathrm{Cu}(111)$ sample was cleaned by several cycles of Ar sputtering at 1 kV followed by annealing at $400{ }^{\circ} \mathrm{C}$. The quality of the surface was checked by Low Energy Electron Diffraction (LEED) and by the position of the bottom of the surface state as measured by ARPES. A bandmap with the surface state is shown in Fig. VI(a) for $\pi$ polarized $h \nu=21 \mathrm{eV}$. In Fig. VI(b) a spin-resolved MDC of the surface state performed close to the Fermi level is shown. Note that in the absence of any impurity scattering ${ }^{34}$ only a Rashba-type spin splitting is observed.


FIG. VI. (a) Bandmap of the surface state of $\mathrm{Cu}(111)$ measured with $h \nu=21 \mathrm{eV}$; (b) spin-resolved MDC of the surface state close to the Fermi level, $\pi$ polarized $h \nu=21 \mathrm{eV}$.

## II.B. Comparison with $\mathrm{Au}(111)$

Under inversion symmetry breaking, time-reversal symmetry alone cannot guarantee the Kramers degeneracy, and thus the spin degeneracy is lifted as a function of momentum resulting into two spin polarized states. Since the presence of a surface itself implies inversion symmetry breaking, electronic surface states experience the so-called Rashba splitting ${ }^{13}$, as it was shown in Fig. VI. In some materials, where there is no inversion symmetry because of their crystal structure, also the bulk states will experience Rashba splitting ${ }^{27,28}$. This is however not the case of $\mathrm{Cu}(111)$, since its crystal structure is inversion symmetric. Nevertheless, a bulk state can still be splitted because of the combined strong influence of the surface on the bulk band structure and the surface sensitivity of photoemission ${ }^{35,36}$.

We can rule out this effect since it should bring to a much larger splitting in a stronger spin-orbit coupling material. In Fig. VII a spin-resolved MDC performed on $\mathrm{Au}(111)$ is shown. The results are similar to the one in $\mathrm{Cu}(111)$, thus suggesting that a surface-induced bulk Rashba splitting is not the main cause of spin polarization of the photoelectrons.


FIG. VII. $\mathrm{Au}(111)$ : spin-resolved MDC 0.2 eV below the Fermi level, $\pi$ polarized $h \nu=40 \mathrm{eV}$.

## II.C. Spin-resolved EDCs of the $3 p$ core levels

A survey of spin-resolved EDCs over the $\mathrm{Cu} 3 p$ core levels is shown in Fig. VIII. The $3 p$ level is spin-orbit split into $3 p_{1 / 2}\left(E_{b}=77.3 \mathrm{eV}\right)$ and $3 p_{3 / 2}\left(E_{b}=75.1 \mathrm{eV}\right)$. Because of the strong localization of the core levels the spin polarization is expected to follow the atomic photoionization model. This measurement has been already performed in the past ${ }^{38}$, but only the component relevant to atomic symmetry was considered (the one that corresponds to $P_{y}$ in our setup), and the other two were said to be zero.

In Fig. VIII(a) also $P_{x}$ shows a certain degree of polarization, confirming that the orientation of the spin polarization vector in crystals does not strictly follow the symmetry requirement of isotropic atomic targets. The three angles $\theta_{1,2,3}$ correspond to the $\Gamma$ point (normal emission) and the $k_{\|}$at which the $s p$ band crosses the Fermi level for the two photon energies 130 eV and 46 eV respectively. The three measurements are equivalent within the experimental resolution. Therefore we can conclude that the spin polarization discussed in the main text (measured at $\theta_{2,3}$ ) is not affected by diffraction through the surface effects, since these effects should vanish at normal emission $\left(\theta_{1}\right)$.

In Fig. VIII(b) the two photon energy $h \nu=130 \mathrm{eV}$ and $h \nu=203 \mathrm{eV}$ are compared, which correspond to about the same $E_{k}$ of the experiment performed on the CB at $h \nu=46 \mathrm{eV}$ and $h \nu=130 \mathrm{eV}$, respectively. For a very large difference in $E_{k}$ the change in polarization is only in $P_{y}$ and less than a factor of 2 . This suggest that the dependence of inelastic scattering is not the main cause of spin polarization. Further studies might clarify this point.


FIG. VIII. Spin-resolved EDCs over the $\mathrm{Cu}(111) 3 p$ core levels as a function of (a) $\theta$ ( $h \nu=130 \mathrm{eV}$ ) and (b) $h \nu\left(\theta=\theta_{2}\right)$.

## III. COMMENT IN RELATION TO THE HEISENBERG'S UNCERTAINTY PRINCIPLE

The Heisenberg uncertainty relationships do not affect our measurement of a time-delay. In fact, the well-known energy-time relationship:

$$
\begin{equation*}
\Delta E \Delta t \geq \frac{\hbar}{2} \tag{S7}
\end{equation*}
$$

even if it is commonly referred to as an Heisenberg uncertainty relationship, it only is a general property of Fourier transformation. Since time is not an operator in (non-relativistic) quantum mechanics, it is not an observable ${ }^{29}$, and thus it is not limited by Heisenberg relationships. A better quantum formulation of the energy-time relationship is ${ }^{30}$ :

$$
\begin{equation*}
\sigma_{\hat{H}} \sigma_{\hat{Q}} \geq \frac{\hbar}{2}\left|\frac{d\langle\hat{Q}\rangle}{d t}\right| \tag{S8}
\end{equation*}
$$

where $\sigma$ represents the standard deviation, $\hat{H}$ is the Hamiltonian operator of the system and $\hat{Q}$ is any observable not explicitly dependent on time. Defining $\Delta E=\sigma_{\hat{H}}$ and $\Delta t=\sigma_{\hat{Q}} /\left|\frac{d\langle\hat{Q}\rangle}{d t}\right|$ one then obtains eq. (S7). From eq. (S8) it follows that for a given uncertainty $\sigma_{\hat{H}}$ the uncertainty of any observable $\sigma_{\hat{Q}}$ is related to the change in time of the expectation value of the observable itself. In other words, the rate of change of any observable must be slow enough in order to have a good resolution in both $\langle\hat{H}\rangle$ and $\langle\hat{Q}\rangle$, which does not set any restriction at all to the value of a measured time-delay itself.

Another reason that allows us to access the time-delay from the spin polarization even by maintaining a good energy resolution, is that the spin polarization measured with SARPES is a measurement carried over an ensemble of electrons, each of them being photoemitted under the very same conditions, and not for a single particle. For the very same reason it is possible to measure with SARPES the spin polarization vector in the three dimensions, which is an information about the photoelectron beam ensemble: it doesn't mean that it is possible to measure at the same time the projection of the spin vector on three orthogonal directions.
${ }^{13}$ J. H. Dil, Journal of Physics: Condensed Matter 21, 403001 (2009).
${ }^{14}$ J. Kessler, Polarized Electrons, 2nd edition. (Springer, Berlin Heidelberg, 1985).
${ }^{25}$ E. Tamura and R. Feder, Solid State Communications 79, 989 (1991).
${ }^{26}$ E. Tamura and R. Feder, Europhys. Lett. 16, 695 (1991).
${ }^{27}$ K. Ishizaka, M. S. Bahramy, H. Murakawa, M. Sakano, T. Shimojima, T. Sonobe, K. Koizumi, S. Shin, H. Miyahara, A. Kimura, K. Miyamoto, T. Okuda, H. Namatame, M. Taniguchi, R. Arita, N. Nagaosa, K. Kobayashi, Y. Murakami, R. Kumai, Y. Kaneko, Y. Onose, and Y. Tokura, Nat. Mat. 10, 521 (2011).
${ }^{28}$ G. Landolt, S. V. Eremeev, Y. M. Koroteev, B. Slomski, S. Muff, T. Neupert, M. Kobayashi, V. N. Strocov, T. Schmitt, Z. S. Aliev, M. B. Babanly, I. R. Amiraslanov, E. V. Chulkov, J. Osterwalder, and J. H. Dil, Phys. Rev. Lett. 109, 116403 (2012).
${ }^{29}$ P. Busch, Foundations of Physics 20, 1 (1990).
${ }^{30}$ D. Griffiths, Introduction to quantum mechanics (Prentice Hall, Englewood Cliffs, N.J, 1995).
${ }^{34}$ J. H. Dil, F. Meier, and J. Osterwalder, Journal of Electron Spectroscopy and Related Phenomena 201, 42 (2015).
35 A. Kimura, E. E. Krasovskii, R. Nishimura, K. Miyamoto, T. Kadono, K. Kanomaru, E. V. Chulkov, G. Bihlmayer, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. 105, 076804 (2010).
${ }^{36}$ S. N. P. Wissing, C. Eibl, A. Zumbülte, A. B. Schmidt, J. Braun, J. Minár, H. Ebert, and M. Donath, New Journal of Physics 15, 105001 (2013).
${ }^{38}$ C. Roth, F. U. Hillebrecht, W. G. Park, H. B. Rose, and E. Kisker, Phys. Rev. Lett. 73, 1963 (1994).

