Natural linewidth analysis of d-band photoemission from Ag(110)

A. Gerlach, K. Berge, T. Michalke, and A. Goldmann

Fachbereich Physik, Universität Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

C. Janowitz and R. Müller

Institut für Physik, Humboldt-Universität zu Berlin, Invalidenstr. 110, D-10115 Berlin, Germany

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We report a high-resolution angle-resolved study of photoemission linewidths observed for Ag(110). A careful data analysis yields k-resolved upper limits for the inverse inelastic lifetimes of d-holes at the X-point of the bulk band structure. At the upper d-band edge the hole-lifetime is \( \tau_h \geq 22 \) fs, i.e. more than one order of magnitude larger than predicted for a free-electron gas. Following calculations for d-hole dynamics in Cu (I. Campillo et al., Phys. Rev. Lett., in press) we interpret the lifetime enhancement by a small scattering cross-section of d- and sp-states below the Fermi level. With increasing distance to \( E_F \) the d-hole lifetimes get shorter because of the rapidly increasing density of d-states and contributions of intra-d-band scattering processes, but remain clearly above free-electron-model predictions.

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I. INTRODUCTION

The dynamics of excited electrons at metal surfaces plays a key role in understanding basic processes like chemical reactions at surfaces and transient magnetization effects on a femtosecond time-scale. While this time regime is now accessible by ultrashort laser pulse pump-probe techniques, which for example allow to determine the occupation time of the intermediate level with high precision, the detailed interpretation of such results has generated considerable controversy. The underlying problem is easily recognized: The observed energy relaxation times do not represent the lifetime of a single excited electron, but result from a convolution of several complex and not yet well understood occupation/decay-channels like capture of time-delayed secondary electrons and removal of electrons by ballistic transport out of the region probed experimentally. Therefore a basic understanding of all steps involved is required.

In this context low-index surfaces of the noble metals have been investigated very detailed both experimentally and theoretically. The experimental data for excited state electron lifetimes of copper at energies above \( E_F \) show an unexpected dependence on distance from \( E_F \), on photon energy and laser pulse duration. The intermediate state lifetime probed by pulse-probe techniques exhibits a peak just above the threshold for excitation of d-holes. The dispute is whether or not the delayed decay of d-holes via an Auger process is responsible for the apparent increase of lifetime within the observed peak. The recent calculations by Knorren et al. are able to model this peak quantitatively by including the contributions of photoexcitation, electron-electron scattering, secondary electrons generated both from scattering cascades and Auger decay of d-holes, and finally transport of excited carriers out of the detection region. Their model is based, however, on the Boltzmann equation which uses the d-hole lifetime \( \tau_h \) as an adjustable parameter, with \( \tau_h = 35 \) fs.

In this context an independent determination of d-hole lifetimes is highly desired. Up to now only few studies have attempted to measure such data. Lower bounds of \( \tau_h = 24 \) fs and \( \tau_h = 26 \) fs have been reported at the top of the Cu d-bands. Therefore we have started a systematic investigation of d-hole lifetimes in noble metals using natural-linewidth analysis of high-resolution angle-resolved one-photon photoemission spectra. Data for several well-defined k-space points within the Cu bulk band structure have been reported elsewhere. To check for systematic trends we extend our studies to the isostructural and isoelectronic surfaces of Ag. In the present paper we report new high-resolution data for Ag(110), and discuss them in the context of available knowledge.

II. EXPERIMENTAL DETAILS

The experiments with synchrotron radiation were performed at the storage ring Bessy I in Berlin. Normal-emission photoelectron spectra were collected using the 2m-Seya beamline and a high-resolution photoemission station described and characterized in detail in Ref. 11. The sample is mounted on a manipulator cryostat having five degrees of freedom: x-, y-,z-translation, rotation around the manipulator axis and rotation around the surface normal. The
sample temperature could be varied between 20 K and room temperature. A sample load lock system with a transfer rod allows to decouple the sample from the manipulator for preparation by argon ion bombardment and annealing. The energy resolution including the photon monochromator was in most cases set to $\Delta E = 27 \pm 5$ meV as verified by the analysis of the Fermi edge emission taken at $T = 22$ K. Angular resolution was $\Delta \theta = \pm 1^\circ$, which is sufficient for normal emission spectra taken at flat bands, i.e. just at symmetry points. The Ag(110) crystal was oriented to $\pm 0.25^\circ$. It was 1.5 mm thick and had a diameter of about 10 mm. Its high surface quality was characterized before by experiments in our home laboratory, using a SCIENTA high-resolution photoelectron spectrometer. In these measurements we obtained very sharp LEED spot profiles and, even more relevant, a sharp photoemission peak from the Shockley-type surface state residing at an initial state energy $E_i = -0.055$ eV at $T = 300$ K. These observations indicate that no significant linewidth broadening due to defect scattering is to be expected for the data presented below.

### III. RESULTS

#### A. Measuring hole-lifetimes

The spectral linewidth of a photoemission peak is generally determined by both the lifetime of the photohole and the excited state electron lifetime. In fact the linewidth is very often dominated by the final state contribution. There are only two situations where the hole-lifetime is reflected directly in the experimental width $\Gamma_{\text{exp}}$: Either the relevant photoemission initial state does not depend on $k_{||}$, the electron wave vector component perpendicular to the surface (as is the case for 2D surface bands) or the transition starts at symmetry points $E_i(\bar{k})$ of the 3D bulk bands, where the band velocity $v = \hbar^{-1} | \partial E / \partial k |$ is zero. To be more quantitative the measured linewidth is given by

$$\Gamma_{\text{exp}} = \left( \Gamma_h + \frac{v_h}{v_e} \Gamma_e \right) \left( 1 - \frac{v_h}{v_e} \right)^{-1},$$

where $\Gamma_h, \Gamma_e$ are the final state hole and electron inverse lifetimes $\Gamma = \hbar / \tau$ and $v_h, v_e$ are the corresponding band velocities. The detailed theory of photoemission, using rigorous perturbation theory and incorporating $\Gamma_h$ and $\Gamma_e$ in the relevant transition matrix elements, shows that an isolated emission peak has a Lorentzian lineshape, provided initial and final state disperse linearly across the peak and a quasiparticle description is appropriate. In what follows we take normal emission spectra from Ag(110) at different photon energies $\hbar \omega$, thereby tuning the photoelectron transitions to $k$-space points around the X-point of the ΓKX-direction parallel to the surface normal. At X, where $v_{||} = 0$ eqn. (1) results in $\Gamma_{\text{exp}} = \Gamma_h$. Additional mechanisms beyond hole decay may contribute to the linewidth, e.g. from final state excitations. The most important one is the hole-phonon interaction, which increases $\Gamma_{\text{exp}}$ linearly with temperature $T$, except at very low temperatures. By adequate extrapolation of our results to $T \to 0$ we finally end up with an experimental upper limit for the inverse hole lifetime $\hbar / \tau_h$.

#### B. Data analysis

We have collected normal emission spectra from Ag(110) for photon energies between $\hbar \omega = 10.2$ eV and 29.0 eV, both at room temperature and $T = 22$ K. The upper panel of Fig. 1 shows two spectra taken at $T = 300$ K, with $\hbar \omega = 15.3$ eV (solid line) and $\hbar \omega = 19.0$ eV (dashed curve). These data were each normalized to the photon flux via the current obtained from the last monochromator mirror. Obviously strong intensity changes occur with variation of $\hbar \omega$ which will be discussed further below. The bottom of Fig. 1 shows an enlarged part of the data taken at 15.3 eV, together with three fit-curves based on a Lorentzian line shape. Three peaks 3...5 are clearly resolved which correspond to emission from bulk $k$-space points near $X_7^+, X_6^+$ and $X_7^+$, compare the band structure shown in Fig. 2. Peak 1 (upper panel) results from a direct transition out of the bottom band between K and X.

From fits like those shown in Fig. 1 we obtain peak positions as summarized in Fig. 3. As expected different photon energies are necessary to induce transitions at the X-point: The three upper $d$-bands around $E_i = -4$ eV reach the critical point at $\hbar \omega = 15.3$ eV, easily identified by the smallest binding energy $|E_i|$ in each band. In contrast the lowest $d$-band is probed at the X-point with photons of $\hbar \omega = 19.0$ eV, corresponding to the greatest binding energy $|E_i|$. Our data resolve only one peak from bands 1 and 2 near X. This is consistent with earlier work: Wern et al. report a splitting of 60 meV between $X_{6^+}$ and $X_{7^+}$, as deduced from data collected at the Ag(100) surface. Such a small splitting cannot be resolved in our normal-emission spectra from Ag(110), because the lifetime broadening exceeds the band splitting considerably, see below for details. Our results for the various X-point
FIG. 1: Top: Normal-emission photoelectron spectra taken at room temperature from Ag(110) with photons of energy $h\omega = 15.3\,\text{eV}$ (solid line) and $19.0\,\text{eV}$ (dotted). Note that both curves refer to the same intensity scale, obtained by normalization to the last-mirror current of the monochromator. Peak numbers refer to data collected in table 1. Bottom: Decomposition of peaks 3 to 5 using three Lorentzians and a linear background (not shown). All energies given with respect to $E_F$.

Figures 1.

From peak fits based on Lorentzians we can also determine the relative intensities (area below peak) and the widths of the photoemission lines in their dependence on the photon energy $h\omega$. These results are summarized in Fig. 3. Obviously the intensities show a sudden drop at photon energies above $15\ldots16\,\text{eV}$ (top panel). The interpretation results from closer inspection of the band structure in Fig. 2. Below $h\omega = 15\,\text{eV}$ the photoemission peaks 3\ldots5 are due to direct transitions from initial bands 3\ldots5 to the final state band 8, which carries essentially “free-electron-like” character, i.e. in its wave-function the amplitude of the partial plane wave $\exp[i(\vec{k} + \vec{G}(110)) \cdot \vec{r}]$. The energies are collected in table 1. Where comparable our results are in excellent agreement with earlier band structure investigations of Ag\cite{22,23}, see also table 7.2 in Ref. 15.
FIG. 2: Bulk band structure of Ag calculated by Eckardt et al. along the ΓKX-direction of the Brillouin zone. The bands have been labeled 1...11 counted from the lowest band below $E_F$ up to the highest energy above $E_F$. Note different energy scales above and below $E_F$. 
FIG. 3: Initial state energies $E_i(h\omega)$ observed in normal emission from Ag(110) in their dependence on photon energy $h\omega$. Numbers 1...5 refer to initial state bands as labeled in Fig. 2.

is dominant. This is the “primary cone emission” using Mahan's terminology, i.e. the final-state group velocity is directed along the surface normal, with a concomitant high peak intensity. At $h\omega = 15.3$ eV, however, the transition starting at the X-point from band 5 (arrow A in Fig. 2) ends at the lower edge of a gap opening between $X_6$- and $X_{7+}$ (final state energy $E_f = 10.9 \ldots 17.1$ eV). Therefore transitions with $h\omega = 19.0$ eV from initial states with $E_i \approx -4$ eV near the X-point end within the gap (arrow B in Fig. 2) and no direct (vertical) transition is allowed. Hence only “surface emission” (for more details see chapters 6.3.3 and 7.3.4 of Ref. 15) is possible, which conserves $k_\parallel$ only. The emission occurs via evanescent states located energetically within the gap and one measures approximately a one-dimensionally $k_\parallel$-resolved bulk density of initial states. Consequently not only intensities are affected (top panel of Fig. 3) but also the positions of peak 3...5 (Fig. 3) remain essentially constant for transitions into the gap region, i.e. at photon energies between about 16 eV and 23 eV (arrow C in Fig. 2). At $h\omega > 23$ eV, direct transition are possible into band 11 and band dispersion to larger $|E_i|$ is seen again in peaks 3...5 (Fig. 3). A very similar
behaviour, both with respect to photon energy dependence of intensities and of experimentally observed initial state energies, had already been observed for normal emission from the Cu(110) surface. This is not surprising, because Cu is isoelectronic and isostructural to Ag and exhibits a similar band structure, with a final state gap between about 15 and 20 eV above $E_F$. 

**FIG. 4:** Top: Intensity variation of emission peaks (labeled according to initial bands as numbered in Fig. 2) as a function of $\bar{h}\omega$. Relative intensities obtained by normalization of count-rates to last-mirror current of the monochromator. Note that the ordinate scale is logarithmic. Bottom: Full-width at half-maximum of the Lorentzians used to decompose the experimental spectra.

Spectra with $\bar{h}\omega$ adjusted to initial states at the X-point were also taken as a function of sample temperature. Two results are of relevance in our context. Firstly the three initial state energies $E_i$ of peaks 3 ... 5 shift only marginally to larger $|E_i|$ with increasing temperature: $\Delta E_i \leq 20$ meV between $T = 20$ K and 310 K. This unexpectedly small effect results from a compensation of two opposite trends: With increasing temperature the lattice expands and the initial bands should move upwards in Fig. 2. Simultaneously, however, the $d$-bands experience reduced wave-function
overlap, and this decreases the overall $d$-band width. Similar compensation has also been observed at the X-point for Cu, and the interpretation was based on band-structure calculations for Cu at different lattice constant to simulate thermal expansion. The second temperature effect is a linear increase in half-width of peaks 3 and 4, see Fig. 5. Its origin is the hole-phonon ($h - ph$) interaction. If we parameterize the increment in width according to $\Gamma_{h-ph} = 2\pi\lambda k_B T$, we obtain $\lambda = 0.58$ (peak 3) and $\lambda = 0.34$ (peak 4), respectively, with an estimated error smaller than 15%. Any phonon contribution to the width of peak 5 is obviously below our experimental uncertainty of $\pm 10$ meV (corresponding to $\lambda < 0.15$).

Table 1 finally shows the experimental line-widths $\Gamma_h$ as well as the corresponding hole lifetimes $\bar{h}/\Gamma_h$ after the extrapolation to $T \to 0$ and a correction for the experimental energy resolution. Additionally all data for $\Gamma_h$ are reproduced in Fig. 6, which will be discussed further below. As mentioned already, peak 1 is a double-peak, resulting from two transitions about 60 meV apart. We have assumed equal intensity from both $d$-like initial states $X_6^+$ and $X_7^+$ and subtracted 60 meV from the experimental line-width. This data is then shown in table 1 and in Fig. 6.

C. Line shape analysis

Closer inspection of Fig. 5 (bottom) shows that the right wing of peak 5 is not adequately modeled by the shape of the Lorentzian. This is not surprising, because there are at least two questionable assumptions in this description: Firstly Lorentzian line shape results only if both the initial and the final state bands disperse linearly across the direct transition photoemission peak. In our case this condition is clearly violated at the X-point, compare Fig. 2. Secondly $\Gamma_h$ and $\Gamma_e$ were treated as constant within a spectral line. From a theorists point of view $\Gamma_h$ and $\Gamma_e$ are the imaginary parts of the self-energy which themselves depend on energy and momentum. Especially at the upper

![Figure 5: Experimental width (FWHM) of peaks 3...5 of Fig. 1 as a function of sample temperature.](image)

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TABLE I: Upper limits for $d$-hole lifetimes $\tau_h$ due to electron-hole interaction at various symmetry points of the silver bulk bands. Peak $q$ is observed in Ref. 20 at $\hbar\omega = 12$ eV in normal emission from Ag layers deposited on Fe(100) and results from a $d$-like quantum-well state. Two results from our work are shown for peak 5: The first line is obtained from Fig. 1, the second line from the detailed peak shape analysis as described in the text.

| Peak | Symmetry | $E_i$ [eV] | $\Gamma_h$ [meV] | $\tau_h$ [fs] |
|------|----------|------------|-----------------|--------------|
| 1    | $X_{6+}, X_{7+}$ | -7.43 | 300 ± 40 | 2 |
| 3    | $X_{7+}$ | -4.31 | 143 ± 20 | 5 |
| 4    | $X_{6+}$ | -4.07 | 129 ± 20 | 5 |
| 5    | $X_{7+}$ | -3.76 | 58 ± 10 | 11 |
| 5    | $X_{7+}$ | -3.70 | 30 ± 10 | 22 |
| $q$  | $\Gamma$ | -3.75 | 13 | 51 |

$\hbar/\tau = 2.51 r_s^{5/2} (E-E_f)^2$ [meV]

FIG. 6: Experimental inverse $d$-hole lifetimes obtained for Ag (open circles, this work) and for Cu (open squares, from Ref. 10) at the X-point of the bulk band structure, compare also table 1. The parabolas show calculations for Cu and Ag based on the free-electron gas (equ. (6)). The filled circle for Ag results from a detailed line shape analysis (see text for details). The cross was obtained in Ref. 20 from a $d$-like quantum-well state observed in normal emission from Ag layers on Fe(100).

d-band edge there might be a significant variation of $\Gamma_h$ as suggested by our data in Fig. 6. Therefore we have performed a numerical line shape calculation following the ideas outlined in more detail in subsections 3.2 to 3.4 of Ref. 14.

The basic strategy is as follows. The initial state bands $E_i(\vec{k})$ are taken from the calculation of Ref. 21. In order to improve the agreement with the experimental spectral line at $E_i = -3.76$ eV they were rigidly shifted downwards by 70 meV. The final state is modeled by a free-electron-like band according to $E_f(k_\perp) = V_0 + \hbar^2 k_\perp^2/2m$, where
m is the free electron rest mass. We have chosen $V_0 = -6.5\text{eV}$ such that the X-point is crossed at $\hbar \omega = 15.3\text{eV}$ when considering peak 5. We note, however, that a variation of $V_0$ by 1eV does not change the results within our accuracy. The empirical bridging of the final state gap by a free-electron-like band has been justified in many earlier studies, see e.g. Refs. 27, 28, 29 and many references listed in Ref. 14. The finite escape length of photoelectrons is equivalent to a damping, i.e. a non-zero imaginary part of the lattice potential, which results in a complex $k$-vector.\footnote{\textsuperscript{23}} A sufficiently strong damping makes the gap almost disappear and thereby gives rise to bands with an approximated free-electron-like shape.\footnote{\textsuperscript{23}} This assumption has been verified for Ag(110) in an earlier experimental investigation.\footnote{\textsuperscript{23}} Since we only intend to model the shape of the peaks we assume the photoemission matrix element, which connects free-electron-like shape \footnote{\textsuperscript{27}}\footnote{\textsuperscript{28}}\footnote{\textsuperscript{29}} the integration given by equ. (2) the resulting half-maximum. They are treated as parameters in order to reproduce the experimental line shape. After performing of hole-lifetime effects and integration over a finite $k$-range around the X-point the particular choice of $\Gamma_k$ mainly influences the left wing of peak 5.

The line shape $I(E_i)$ is then given for each contributing transition by the convolution (equ. (20) of Ref. 14)

$$I(E_i) \propto \int dk_\perp L_h(E_f - E_i - \hbar \omega, \sigma_h) L_e(k_\perp^0 - k_\perp - G_\perp, \sigma_e).$$ \hspace{1cm} (2)

In equ. (2) $L_h$ and $L_e$ are Lorentzian distributions, whereas $\sigma_h$ and $\sigma_e$ represent the corresponding half-widths at half-maximum. They are treated as parameters in order to reproduce the experimental line shape. After performing the integration given by equ. (3) the resulting $I(E_i)$ is additionally convoluted with a Gaussian to account for the experimental energy resolution before comparison with the measured line shape. To model $\sigma_h$ we have chosen

$$\sigma_h(E_i) = 71 (|E_i| - 3.70)^{1/2} + 15 \text{[meV]}$$ \hspace{1cm} (3)

for the energy range $E_i < -3.70\text{eV}$. Above the upper d-band edge, i.e. $E_i > -3.70\text{eV}$, we simply assume $\sigma_h = 15\text{meV}$. Our choice of $2\sigma_h = \Gamma_h$ is reproduced as the solid line drawn through the FWHM results for Ag (open circles) in Fig. 6 and assumes that $\Gamma_h$ does not change significantly with $k_\perp$ in the vicinity of the X-point. This parameterization, however, implies a drastic decrease of $\Gamma_h$ on approaching the d-band edge. For the corresponding final states we use

$$\sigma_e(E_f) = \frac{dk_\perp}{dE_f} \Gamma_e,$$ \hspace{1cm} (4)

where $E_f$ is the free-electron-like parabola mentioned above. The linear relation

$$\Gamma_e = a(E_f - E_F)$$ \hspace{1cm} (5)

used in our calculation is an empirical average over many photoemission results, see Ref. 31 for experimental data and Ref. 3 for some theoretical background. Due to the dispersion of bands 3...5 around the X-point the particular choice of $a$ mainly influences the left wing of peak 5.

Typical results of the numerical integration following equations (2) to (3) with $a = 0.13$ and $a = 0.20$ are shown in Fig. 3. Most insight is obtained by considering the asymmetric peak 5 at the top of the d-bands. Obviously the right wing of this peak is reproduced almost perfectly in both cases. In particular the agreement of the data points and the calculated peak (solid line) between $E_i = -3.5\text{eV}$ and peak maximum is very much improved by our choice of $\sigma_h(E_i)$ in this energy range compared with the data shown in the bottom panel of Fig. 3. A satisfying fit results with $a = 0.13$ (top panel of Fig. 3), whereas $a = 0.20$ overestimates the asymmetry of peak 5 (bottom panel). Similarly, calculations with $a < 0.13$ get the FWHM too small. We have performed several calculations varying also the other line-width parameters. Our conclusions may be summarized as follows. At the upper d-band edge we observe a significant decrease of $\Gamma_h$, which is consistent with the measured line shape. Consequently we get $\Gamma_h = 30 \pm 10\text{meV}$ at $E_i = -3.70\text{eV}$ as upper limit. The final state damping for energies $E_f - E_F = 10 \ldots 12\text{eV}$ is readily described with $a = 0.13 \pm 0.03$. This number is in perfect agreement with our earlier result obtained from an average over several metals.\footnote{\textsuperscript{23}} In particular our analysis of peak 5 reveals that the asymmetric line shape is due to a combination of hole-lifetime effects and integration over a finite $k_\perp$-range around the X-point caused by the electron-lifetime broadening of the final state. Any variation of $\Gamma_h(E_i)$ with $k_\perp$ in the vicinity of the X-point is below our limits of detection. Moreover, the line shape analysis of peak 5 is consistent with an only small contribution to the linewidth of less than 15meV from scattering interactions with structural defects.

IV. DISCUSSION

For many years the theory of quasiparticle lifetimes was based on free-electron model calculations. Within this framework the inelastic lifetime of hot electrons ($E > E_F$) as well as holes ($E < E_F$) is approximately given by

$$\tau = 263 \tau_s^{-5/2} (E - E_F)^{-2} \text{fs eV}^2,$$ \hspace{1cm} (6)
FIG. 7: Results from line shape analysis at the X-point using different broadening parameters for the photoelectron final state. See text for details.

where the electron density parameter $r_s$ is defined by the relation $1/n_0 = 4\pi (r_s a_0^3)/3$ with the electron density $n_0$ and $a_0$ being the Bohr radius. The strict validity of equ. (6), however, is limited to energies close to $E_F$. For comparison with experimental data we have plotted $\hbar/\tau$ according to equ. (6) for Ag ($r_s = 3.01$) and Cu ($r_s = 2.67$) in Fig. Also included in this figure are the experimental results for Cu from Ref. The observed linewidths both for Cu and Ag are clearly below the free-electron predictions. As is evident, both experimental data sets show a close similarity. Particularly at energies near the top of the $d$-bands the natural linewidth deviate drastically from the quadratic energy dependence predicted by equ. (6). This threshold-like behaviour has been first observed for Cu in time-resolved two-photon photoemission and was verified subsequently in one-photon photoemission experiments.

We are not aware of any ab-initio calculations for lifetimes of $d$-holes in Ag. Nevertheless several first-principles calculations based on the very details of the electronic band structure have shown that the lifetimes generally result from a delicate balance between density of states, localization of electrons and dynamical screening. In this
context Cu and Ag show some remarkable differences: Due to the additional participation of the Ag 4d states in the screening of the photohole longer lifetimes might be expected. However, our results demonstrate that this effect is compensated. Since the d-bands of Ag are located at $E_i \leq -3.75 \text{eV}$, i.e. almost 2 eV lower than in Cu, the enlarged phase space of sp-electrons available for hole-scattering shortens the lifetimes within the d-bands. This scattering should even be more effective in Ag compared to Cu, because the Ag 4d electrons experience a stronger delocalization. The measured relaxation times of hot electrons in Ag with $E - E_F < 3.7 \text{eV}$ essentially follow the energy dependence predicted by the free-electron model. Especially the characteristic long lifetimes of noble metals, i.e. 50 fs at 1 eV above the Fermi level, are observed. Due to the large threshold for creation of d-holes these electrons do not show up in time-resolved photoemission.

The hot electron and hole-dynamics has recently been analyzed for Cu and Au by means of first-principles many-body calculations taking the d-bands explicitly into account. In agreement with the experiment these results indicate that d-holes in Cu and Au exhibit larger inelastic lifetimes than excited sp-electrons at corresponding distance from $E_F$. This enhancement is in particular strong at the upper d-band edge, i.e. the threshold for creation of d-holes. The underlying physics is as follows. While the density of states available for d-hole decay is larger than that for the decay of excited electrons (this should shorten the lifetimes) the scattering cross-section of d- and sp-states below $E_F$ is very small at the top of the d-bands, and this considerably decreases the decay rates. With increasing distance to $E_F$ ($E_i < -2 \text{eV}$ in Cu) the phase space for the hole to decay increases and, simultaneously, the cross-section for hole-scattering within the d-bands gets larger. In consequence the linewidths increase below the upper d-band edge, in agreement with the experimental data shown in Fig. II.

As mentioned already, calculations are available for Cu only. At present a quantitative comparison of experiment and theory is still difficult because of two critical discrepancies: Firstly these calculations get the d-bands rigidly shifted up by 0.5 eV as compared to experiment. Secondly the calculated decay rates usually represent an average over all wave vectors and electron bands referring to the same initial state energy. There is one exception, however. At the top of the Cu d-bands, at the X5 point (calculated at $E_i = -1.5 \text{eV}$) and with the k-vector along the ΓX-direction, theory obtains a d-hole lifetime of 99 fs. This has to be compared to the k-space averaged value of 72 fs at the same energy below $E_F$. The lifetime of $\tau = 99 \text{fs}$ corresponds to a predicted photoemission linewidth $\Gamma_h = 7 \text{meV}$ at $X_5$, which is clearly compatible with the experimental upper limit of Fig. III, i.e. $\Gamma_h \leq 25 \text{meV}$. We also mention in this context that our result for the upper d-band edge at of Ag is $\Gamma_h \leq 30 \text{meV}$, and that the quantum well state observed in Ag layers on Fe(100) may be modeled using a lifetime width of $\Gamma_h = 13 \text{meV}$, see the cross in Fig. II. The latter numbers yield $\tau_h \geq 22 \text{fs}$ and $\tau_h \geq 51 \text{fs}$, which data appear reasonable in the light of the Cu calculations.

In summary we have presented a detailed experimental investigation of inverse d-hole lifetimes at the X-point of Ag. The data show a threshold-like behaviour at the upper edge of the d-bands, with unexpectedly long lifetimes $\tau_h \geq 22 \text{fs}$ at 3.70 eV below $E_F$. For deeper lying bands, the experimental $\tau$-values get much smaller, down to 2 fs at 7.43 eV below $E_F$. This trend is similar to what has been observed for copper and demonstrates convincingly that free-electron-like models are not adequate to describe d-hole decay in noble metals. As shown by calculations for Cu the lifetime enhancement at the upper d-band edge results from very small scattering cross-section of d- and sp-states. With increasing distance to $E_F$, the rapidly increasing density of states and intraband scattering enhance the decay rate and thus shorten the d-hole inelastic lifetimes considerably. We hope that our result also stimulates more detailed theoretical work, because quantitative understanding of hole decay is an important ingredient in any attempt to tailor excited electron dynamics.

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* E-mail: agerlach@physik.uni-kassel.de
† E-mail: berge@physik.uni-kassel.de
‡ E-mail: michalke@physik.uni-kassel.de
These values for $r_s$ represent the electron density due to the $sp$-electrons only.