Lifetime of d holes at Cu surfaces: Theory and experiment

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We have investigated the hole dynamics at copper surfaces by high-resolution angle-resolved photoemission experiments and many-body quasiparticle GW calculations. Large deviations from a free-electron-like picture are observed both in the magnitude and the energy dependence of the lifetimes, with a clear indication that holes exhibit longer lifetimes than electrons with the same excitation energy. Our calculations show that the small overlap of d and sp states below the Fermi level is responsible for the observed enhancement. Although there is qualitative good agreement of our theoretical predictions and the measured lifetimes, there still exist some discrepancies pointing to the need for a better description of the actual band structure of the solid.

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I. INTRODUCTION

Electron and hole dynamics in the bulk as well as at the various surfaces of a solid play a key role in a great number of physical and chemical phenomena.1–3 These range from photon-induced surface reactions in metals to device-physical applications in semiconducting nanostructures. It is evident that both reliable experimental information and detailed theoretical understanding are necessary prerequisites for any future application-oriented tailoring of dynamical electronic properties. Seen from theory any excitation of an electron-hole quasiparticle reflects basic properties of the solid as a correlated many-electron system, which must necessarily be described with inclusion of the very details of band structure, symmetry, and dimensionality, and also the various excitation and decay channels. From the experimental point of view, additional contributions to experimental spectra result from effects like coupling of electrons and holes to phonons and their scattering with structural defects, and it is a sometimes tedious task to distinguish these effects unambiguously.4,5

At present our quantitative understanding of the excitation mechanisms and their relaxation channels is far from being complete: There is ample experimental evidence from experiments at copper surfaces6–8 that hot-electron lifetimes \( \tau \) probed by time-resolved two-photon photoemission (TR-TPPE) techniques do not follow an inverse quadratic dependence \( \tau \propto (E - E_F)^{-2} \), which would result from simple phase-space considerations.9 In contrast, an analysis of the standing-wave patterns observed by scanning tunneling spectroscopy on Cu(111) has been shown to yield an accurate quadratic behavior in the same energy range, i.e., up to about 3 eV above the Fermi level \( E_F \).10 In this tunneling experiment electrons are injected into a well-defined surface-state band, and the coherence length \( l \) is then derived from the spatial damping of the standing-wave pattern produced by repeated reflections between parallel steps. Simple and reliable model assumptions connect \( l \) with \( \tau \) and allow the determination of \( \tau (E - E_F) \). TR-TPPE, however, uses femtosecond pump-probe techniques to monitor the time-dependent occupation of the intermediate-energy levels. These may have decay and excitation channels which differ from those of the tunneling experiment. One aspect appears particularly important: Photons with typical energies of 3–4 eV do not only probe sp-like bulk and surface electrons, but in some cases also electrons from occupied d bands are excited.6–8,11 Regarding the above-mentioned TR-TPPE experiments on copper, where the upper edge of the d bands is located 2.0 eV below the Fermi level, a still ongoing debate considers whether7 or not8 Auger recombination of long-lived d holes contributes significantly to the hot-electron generation.

Since neither the magnitude nor the energy dependence of d-hole lifetimes is precisely known, we consider this subject to be of significant current interest. The experimental data for copper presented in this paper were obtained using one-photon photoemission spectroscopy,12,13 This technique allows to determine lifetimes only from a detailed analysis of linewidths,14,15 and requires simultaneously low temperatures, excellent energy, as well as angular resolution, and in general tunable photon energy. This expense is more than compensated for by the very detailed understanding of the one-photon excitation channel and the possibility to locate a photo-hole exactly with respect to both initial-state energy \( E_i \) and wave vector \( \mathbf{k} \). Recent calculations have shown that any reliable theory of hot-electron and hole lifetimes in metals must go beyond a free-electron description of the solid.16–18 In Sec. III of this paper we compare many-body quasiparticle GW calculations of d-hole lifetimes in copper, which have already been presented in Ref. 18, to our photoemission data.

II. EXPERIMENTAL RESULTS

A. Experimental setup

Our 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. 19. The sample is mounted on a manipulator cryostat having five degrees of freedom: $x$, $y$, and $z$ translation; rotation around the manipulator axis; and rotation around the surface normal, the latter one being particularly useful for polarization-dependent suppression of individual photoemission lines. 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 set to 30 meV, as verified by the analysis of the Fermi edge emission taken at $T=22$ K. The angular resolution of $\Delta \theta = \pm 1^\circ$ is sufficient for normal-emission spectra taken at flat bands. The experiments with Cu(100) were performed using a Scienta high-resolution photoelectron spectrometer in our home laboratory. It is equipped with facilities for low-energy electron diffraction (LEED), monochromatized x-ray photoemission spectroscopy, (XPS) and ultraviolet photoemission spectroscopy (UPS), the standard methods for sample cleaning and annealing, and a closed-cycle refrigerator for sample cooling. The spectra reported below were excited using monochromatized HeII radiation ($\hbar \omega = 40.8$ eV) from a Gammatdata microwave light source. The angular resolution was estimated to be about $\pm 0.5^\circ$; the energy resolution was better than 8 meV.

The copper samples were oriented to better than $\pm 0.25^\circ$, polished first mechanically and then electrochemically. After insertion into the UHV chamber they were cleaned and prepared by repeated cycles of argon ion bombardment and an extended annealing procedure at $T=700$ K. The high surface quality had been verified experimentally: In these measurements we obtained very sharp LEED spot profiles of about 1% of the surface Brillouin-zone diameter and, even more significant, sharp photoemission peaks. The Shockley-type surface state on Cu(110), residing at $E_i = -0.43$ eV around the $\bar{Y}$ point,\textsuperscript{12,13} shows a linewidth of less than 80 meV (full width at half maximum) at room temperature. The width of the $d$-like Tamm surface state on Cu(100), residing at $E_i = -1.80$ eV around the $\bar{M}$ point of the corresponding surface Brillouin zone,\textsuperscript{5} is 35 meV at room temperature.

B. Linewidth information

An experimental photoemission linewidth $\Gamma_{exp}$ generally has contributions from both the electron and the hole lifetime. This is discussed in great detail in Ref. 14 (see also Refs. 4,12, and 13). For normal emission, the measured linewidth $\Gamma_{exp}$ is approximately given by

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

where $\Gamma_h = \hbar/\tau_h$, $\Gamma_e = \hbar/\tau_e$ are the final-state hole and electron state inverse lifetimes, and $v_h$, $v_e$ are the corresponding group velocities $v = \hbar^{-1} |\partial E/\partial k|$ taken normal to the surface. Although the copper $d$ bands show a weak dispersion, i.e., $v_x \approx v_y \approx v_h$ (see, e.g., Refs. 4 and 20), the measured linewidth $\Gamma_{exp}$ is generally dominated by the contribution of the photoelectron, because $\Gamma_e$ exceeds $\Gamma_h$ by more than an order of magnitude. In order to obtain $\Gamma_h$, we have to tune the photon energy to direct transitions with $v_h = 0$, i.e., to symmetry points of the band structure along the surface normal. In the experiments with Cu(110) we observed transitions around the X point. At the upper $d$-band edge the bands are split under the combined action of crystal-field and spin-orbit coupling: Three subbands labeled $X_7^+$ ($E_i = -2.00$ eV), $X_6^+ (-2.15$ eV), and $X_7^+ (-2.34$ eV) in relativistic double-group symmetry notation are observed,\textsuperscript{13,20} see inset in Fig. 1. Also at $X_7^+$ ($E_i = -4.80$ eV) a $d$ hole may be created. Direct transitions at the $\Gamma$ point may be excited using photons of $\hbar \omega = 40.8$ eV (HeII radiation) at the Cu(100) surface.\textsuperscript{20} Thus this experiment probes states at $E_i = -3.59$ eV, $\Gamma_{7^+} (-3.40$ eV), and $\Gamma_{7^+} (-2.82$ eV). In summary, we have access to several hole states within the $d$ bands. A determination of their lifetimes by linewidth analysis should be sufficient to recognize trends in $\tau_h(E_i)$.

We collected normal-emission spectra from Cu(110) using photon energies between 14 and 21 eV, both at room temperature and $T=25$ K. A typical spectrum taken at $\hbar \omega = 15.9$ eV and $T=300$ K is reproduced in Fig. 1(a). Four
peaks, which correspond to transitions from k points near $X_{7+}$, $X_{6+}$, $X_{7+}$, and $X_{7+}$, are clearly resolved. Assuming a Shirley-type background to account for the underlying continuous emission and Lorentzian line shapes, all spectra were decomposed in order to obtain the initial-state energy $E_i$, intensity, and linewidth $\Gamma_{\text{exp}}$ in their dependence on $\hbar \omega$. This kind of analysis, as shown in Fig. 1(b), works quite well. But especially peak 1 shows an asymmetric line shape with a broader tail to higher binding energies, which cannot be reproduced by our fit. A detailed line-shape analysis is presented in Ref. 21. We regard the linewidth $\Gamma_h$ at the upper d-band edge and the uncertainty of $k_\perp$ along the $\Sigma$ direction ($\Gamma'_{\Sigma}$), see further below.

Figure 2 shows results for transitions out of the third band below $E_i = -2.34$ eV. The observed peak shift with $\hbar \omega$ is not symmetric around $\hbar \omega = 16.2$ eV, as might be expected from the symmetry along the $\Sigma$ direction in the Brillouin zone. We attribute this to the presence of the well-known band gap above the Fermi level. Photoelectrons excited with $\hbar \omega = 17 - 21$ eV cannot couple to the corresponding bulk states. In consequence, only “surface emission” into evanescent final states contributes to the photoemission intensity, which drops significantly within this photon-energy region. As is evident from Fig. 2(b), the minimum linewidth is obtained at $E_i = -2.34$ eV around $\hbar \omega = 16.2$ eV, i.e., just at the $X_{7+}$ point. This is consistent with Eq. (1). The linewidth $\Gamma_{\text{exp}}$ gets smaller by approaching the X point with $\nu_h = 0$. Similar data were obtained for the other peaks, of course with the maxima and minima located at different photon energies. In the case of peak 1, the experimental resolution exceeds the lifetime width, and our data analysis gets uncertain. Therefore we have taken additional data in our home laboratory using the HeI radiation at $\hbar \omega = 21.2$ eV, which allowed to determine the half width at half maximum of peak 1 at its lower binding-energy side with higher precision. A typical spectrum recorded at $T = 110$ K is reproduced in Fig. 3.

Although the excitation is not exactly related to the X point, the aforementioned band gap “pins” the transition right next to the symmetry point. We regard the linewidth of peak 1 obtained with $\hbar \omega = 21.2$ eV as the upper limit for $\Gamma_h$ with only a small contribution due to the nonvanishing band dispersion.

All linewidths were extrapolated to $T = 0$ K to correct for phonon-induced linewidth contributions $\Gamma_{\text{h-pn}}(T)$. Using the well-known formula

$$\Gamma_{\text{h-pn}}(T) = 2 \pi \hbar \lambda \int_0^\infty d \omega' (\omega'/\omega_d)^2 [1 - f(\omega - \omega')] + 2 n(\omega') + f(\omega + \omega')]$$

where $f(\omega)$ is the Fermi distribution, $n(\omega)$ the Bose distribution and $\hbar \omega_d$ the maximum phonon energy, we derive

$$\Gamma_{\text{h-pn}}(300 \, \text{K}) = 8 \, \text{meV}.$$
taken at three different temperatures are shown in Fig. 4. Being somewhat better resolved than those presented earlier, they demonstrate the dramatic influence of the temperature-dependent broadening due to hole-phonon coupling at the $\Gamma$ point. In practice we never observed any deviation from the linear high-temperature limit of the 3$d$-hole inelastic linewidth due to electron-hole interaction at various symmetry points of the copper bulk band structure. Also reproduced are data obtained at $X_7$ by Purdie et al. (Ref. 28) using high-resolution photoemission from Cu(100) and by Petek et al. (Ref. 29) from TR-TPPE measurements, which are both in excellent agreement with our result.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Peak & Symmetry & $E_i$ & Sample & $\Gamma_{\text{def}}$ & Reference \\
\hline
$X_7$ & $-2.02$ & Cu(100) & $25 \pm 10$ & 28 & \\
$X_7$ & $-1.98$ & Cu(100)/Cs & $28 \pm 3$ & 0.20 & 29 \\
1 & $X_7$ & $-2.00$ & Cu(110) & $21 \pm 5$ & 0.08 & this work \\
2 & $X_6$ & $-2.15$ & Cu(110) & $80 \pm 20$ & this work \\
3 & $X_7$ & $-2.34$ & Cu(110) & $102 \pm 20$ & 0.16 & this work \\
4 & $X_7$ & $-4.80$ & Cu(110) & $232 \pm 30$ & this work \\
5 & $\Gamma_8$ & $-2.82$ & Cu(100) & $132 \pm 20$ & 0.43 & this work \\
6 & $\Gamma_7$ & $-3.40$ & Cu(100) & $177 \pm 30$ & this work \\
7 & $\Gamma_8$ & $-3.59$ & Cu(100) & $152 \pm 20$ & 0.54 & this work \\
\hline
\end{tabular}
\caption{Upper limits for the 3$d$-hole inelastic linewidth $\Gamma_{\text{def}}$ due to electron-hole interaction at various symmetry points of the copper bulk band structure. Also reproduced are data obtained at $X_7$ by Purdie et al. (Ref. 28) using high-resolution photoemission from Cu(100) and by Petek et al. (Ref. 29) from TR-TPPE measurements, which are both in excellent agreement with our result.}
\end{table}

As mentioned already peak 1 cannot be described by a Lorentzian line shape. The steep increase at the low binding-energy side and its clearly visible asymmetry on the opposite wing resembles the Doniach-Sunjic line shape, which is well known for core-level excitation, has a high binding-energy tail due to electron-hole pair excitations around $E_F$. At the $X$ point the $d$ band is flat and one might expect some response of the Fermi sea to the rather well-localized photoelectron peak. Figure 5 shows three different line-shape calculations, which are based on the Doniach-Sunjic formula. The shape of peak 1 cannot be described satisfactorily, if we use an asymmetry parameter $\alpha = 0.05$, which is typically observed in XPS spectra from copper or silver, see the solid line in Fig. 5(a). Although the fit may be improved with $\alpha \gg 0.1$, see Figs. 5(b) and 5(c), one can argue whether these values describe the response function of the $d$ hole. Actually we presume the degree of delocalization to be stronger for the $3d$ bands than for core holes and rule out an exclusive interpretation of the asymmetry due to the Doniach-Sunjic excitation.

Instead we use line-shape modeling going beyond Lorentzians. First, Lorentzian results provided both initial- and final-state bands to disperse linearly across the direct emission photoelectron peak. This is clearly violated at the $X$ point. Second, $\Gamma_{\text{def}}$ is regarded as constant on the energy scale of the linewidth. The data collected in Table I clearly indicate a rapid variation of $\Gamma_{\text{def}}$ around the upper edge of the $d$ band. Therefore we have performed a numerical line-shape calculation following the ideas outlined in detail in subsection 3.2 to 3.4 of Ref. 4. The initial-state bands are taken from the calculation of Ref. 27. The final state is modeled by a free-electron-like band according to $E_k = V_0 + h^2 k^2 / 2m$ where $m$ is the free-electron rest mass and $V_0$ is chosen according to the experimentally observed $x$-point.

The line shape is then given for each contributing transition by the convolution [Eq. (20) of Ref. 4].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.pdf}
\caption{Normal-emission photoelectron spectra, as obtained at different temperatures from Cu(100) with photons of energy $\hbar \omega = 40.8$ eV. Peak numbers refer to data collected in Table I.}
\end{figure}
In Eq. 3 \( I(E_i) \approx \int dk_z \mathcal{L}_h(E_f - E_i - \hbar \omega, \sigma_h) \mathcal{L}_e(k_z - k_z - G_z, \sigma_e). \)  

(3)

In Eq. (3) \( \mathcal{L}_h \) and \( \mathcal{L}_e \) 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 Eq. (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

\[
\sigma_h(E_i) = 64(|E_i| - 1.95)^{1/2} + 10 \text{ [meV]}
\]

(4)

for the energy range \( E_i < -1.95 \text{ eV} \). Above the upper \( d \)-band edge, i.e., \( E_i > -1.95 \text{ eV} \), we simply assume \( \sigma_h = 10 \text{ meV} \).

Our choice of \( 2\sigma_h = \Gamma_h \) assumes that \( \Gamma_h \) does not change significantly with \( k_z \) in the vicinity of the \( X \) point. This parametrization, however, implies a drastic decrease of \( \Gamma_h \) on approaching the \( d \)-band edge. For the corresponding final states we use

\[
\sigma_e(E_f) = \frac{dk_z}{dE_f} \Gamma_e,
\]

(5)

where \( E_f \) is the free-electron-like parabola mentioned above.

The linear relation \( \Gamma_e = a(E_f - E_F) \) used in our calculation is an empirical average over many photoemission results, see Ref. 32 for experimental data and Ref. 9 for some theoretical background. A typical result of the numerically modeled peak shapes together with the parametrization of Eq. (4) is reproduced in Fig. 6. Obviously the agreement is very much improved compared to simple Lorentzians and we believe the resulting data for \( \Gamma_h(E_i) \) around the \( X \) point to be reliable. At the upper \( d \)-band edge we deduce \( \Gamma_h = (20 \pm 5) \text{ meV} \).

On the basis of the experimental linewidth as given in Table I we calculate the corresponding hole lifetimes \( \tau_h = h/\Gamma_h \), which are reproduced in Fig. 7. The lifetime is very
long at the top of the $d$ band ($\tau_h = 31$ fs), then decreases rapidly with increasing distance from $E_F$ and seems to saturate finally. This behavior is clearly not consistent with an energy dependence $\tau_h \propto (E - E_F)^{-2}$. In earlier publications we had collected experimental data taken from spectra measured with laboratory light sources, i.e., without the possibility to tune the photon energy exactly to the symmetry points. These results still seemed to follow the $(E - E_F)^{-2}$ dependence. The corresponding claim, e.g., in Ref. 11 is obviously ruled out by the data. In fact it was Petek and his group who first found the surprisingly long hole lifetime of $\tau_h \approx 24$ fs ($\Gamma_h = 28$ meV) at the upper $d$-band edge, and they also argued that Fermi-liquid-like energy dependence should not hold for the noble metal $d$ holes.

III. THEORETICAL MODEL AND DISCUSSION

For many years the theoretical framework of the $e$-$e$ inelastic lifetimes and mean free paths of excited electrons in metals had been based on the free-electron gas (FEG) model of the solid. In this simple model and for energies very near the Fermi level ($|E - E_F| \ll E_F$), the inelastic lifetime is found to be, in the high-density limit ($r_s \rightarrow 0$), $\tau(E) = 263 r_s^{5/2} (E - E_F)^{-2}$ fs, where $E$ and $E_F$ are expressed in electron volts. Deviations from this simple formula, which have been shown to be mainly due to band-structure effects, were clearly observed. First-principles calculations of the hole dynamics in the noble metals copper and gold have been reported very recently too. Here we focus on the calculation of $d$-hole lifetimes in copper and a comparison with the experiment.

The basic quantity in the investigation of quasiparticle dynamics is the probability per unit time for the probe quasiparticle (electron or hole) to be scattered from a given initial state $\phi_{n,k}(\mathbf{r})$ of energy $E_{n,k}$. In the framework of many-body theory, this probability is identified with the inverse quasiparticle lifetime (we use atomic units, i.e., $\hbar = m_e = 1$),

$$\tau^{-1} = -2 \int d\mathbf{r} \int d\mathbf{r}' \phi_{n,k}(\mathbf{r}) \text{Im} \Sigma(\mathbf{r}, \mathbf{r}'; E_{n,k}) \phi_{n,k}(\mathbf{r}'),$$

(6)

where $\Sigma(\mathbf{r}, \mathbf{r}'; E_{n,k})$ is the so-called self-energy of the quasiparticle. In the GW approximation, one keeps only the first-order term in a series expansion of the self-energy in terms of the screened interaction. For details on further approximations we refer to Ref. 9.

Our full band-structure calculations of hole lifetimes in copper, as obtained from Eq. (6) by averaging over all wave vectors and bands with the same energy, are shown in Fig. 7 (solid circles), together with the FEG calculations with $r_s = 2.67$. There is a qualitatively good agreement of our theoretical calculations and the experimental data, which are both well above the FEG prediction. Band-structure effects, which significantly enhance the lifetimes predicted within a FEG model of the solid, are found to be mainly due to a major contribution from occupied $d$ states participating in the screening of $e$-$e$ interactions, and also to the small overlap of the initial and final $d$-hole and $sp$ states below the Fermi level.

Density-functional theory (DFT) predicts an upper $d$-band edge that is located $\sim 1.5$ eV below the Fermi level, i.e., $\sim 0.5$ eV higher than observed by photoemission experiments. Since the wave functions and energies entering Eq. (6) have been obtained by DFT, the calculation yields enhanced lifetimes at $E = E_F = -1.5$ eV, whereas the measured lifetimes increase near the actual upper $d$-band edge at 2.0 eV below $E_F$, see Fig. 7. As the energy $|E - E_F|$ increases, the larger phase space for the hole decay yields shorter lifetimes, but the small overlap of $d$ and $sp$ states still prevents the establishment of a free-electron-like behavior $\tau \propto (E - E_F)^{-2}$. While our calculated lifetimes below $\sim 3$ eV tend to approach those predicted by a FEG model of the solid, the experimental data show a distinct asymptotic behavior at the large binding energies $|E - E_F|$. This discrepancy between theory and experiment may be, again, due to the failure of the DFT to reproduce the actual band structure of copper. Indeed, experiments and an accurate mapping of the occupied band structure have shown that not only the actual upper $d$-band edge is located $\sim 0.5$ eV lower than predicted by DFT, but also the $d$-band width is 2.7 (1.0) eV at the $X$ ($\Gamma$) point, i.e., $\sim 0.3$ (0.13) eV narrower than in the case of the DFT band structure. This narrowing of the $d$-band points to a stronger decoupling between $d$ and $sp$ states, as well as a localization and hybridization of the states below the Fermi level. Thus the hole lifetimes at the upper $d$-band edge are expected to be even longer than predicted by our calculations. Hence, the departure of the quasiparticle wave functions from their DFT counterparts is expected to prevent the establishment of a free-electron-like behavior, thereby providing a qualitative explanation for the long lifetimes measured below $3$ eV (see Fig. 7).

Comparing the experimental and theoretical data we have to keep in mind that both data sets are not completely compatible: First, theory integrates over the full Brillouin zone, whereas the experimental data refer to selected $k$-space points at $X$ and $\Gamma$. Second, due to the shifted $d$-band edge in the DFT calculation the available phase space for Auger recombination is underestimated, yielding calculated lifetimes which are too long. Third, $sp$-like bands contribute to the calculated data, in particular above the the $d$-band threshold. Finally, the band-structure calculation is performed nonrelativistically, with the symmetry admixtures of different orbital character neglected and splittings due to the spin-orbit coupling at $X$ and $\Gamma$ omitted. Regarding these deficiencies the basic trends are nevertheless well reproduced. There is a thresholdlike onset of large $d$-hole lifetimes at the upper $d$-band edge, both in experiment and theory.

IV. SUMMARY AND CONCLUSIONS

We have presented high-resolution angle-resolved photoemission experiments and many-body quasiparticle GW calculations of $e$-$e$ inelastic lifetimes of $d$ holes in copper. Both our theoretical calculations and the experimental measure-
ments have been found to be well above the FEG predictions, showing the important role that band-structure effects play in the hole-decay mechanism. The $(E - E_F)^{-2}$ dependence of the hole lifetimes is based on the free-electron picture. Flat bands, as occurring near the symmetry points of noble metals, can lead to rather different energy dependence. The experimentally observed decrease of the $d$-hole lifetimes by approximately one order of magnitude within the $d$ bands is attributed to the large phase space and the effective $d$-$d$ scattering. Since the $d$ holes are much more confined to the ionic core, the $d$-$d$ scattering cross section should be much larger than the $d$-$sp$ cross section.

Although there is qualitative good agreement of theory and experiment, there still exist significant discrepancies. On the one hand, both theory and experiment exhibit the longest lifetimes at the top of the $d$ bands, due to the small overlap of $d$ and $sp$ states below the Fermi level. Differences in the position of the maximum lifetime are attributed to the failure of the DFT band-structure calculation. On the other hand the distinct behavior of the lifetimes at large energies $|E - E_F|$ suggest that the narrowing of the $d$-band width may play an important role, thereby showing the need to go beyond DFT in the description of the band structure of copper.

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9 P. M. Echenique, J. M. Pitarke, E. V. Chulkov, and A. Rubio, Chem. Phys. 251, 1 (2000). This review contains many references to earlier work.
33 The parameter $r_1$ is defined by the relation $1/n = 4\pi r_1 a_0^2/3$, $n$ and $a_0$ being the average electron density and the Bohr radius, respectively.
35 The contribution from occupied $d$ states participating in the screening of $e-e$ interactions is also present in the hot-electron decay. However, the low overlap of the hole initial $d$ and final $sp$ states is absent in the case of excited electrons above the Fermi level, which explains the fact that holes exhibit longer
lifetimes than electrons with the same excitation energy.


38 At the top of our calculated DFT $d$ bands, at the $X$ point with $E = -1.5$ eV and $E = -1.7$ eV, we obtain $d$-hole lifetimes of 100 and 90 fs, respectively. These are included as open circles in Fig. 7.