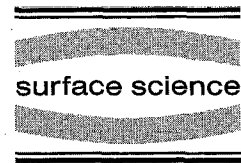




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Lifetime difference of photoexcited electrons between intraband and interband transitions

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Abstract

Using time-resolved two-photon photoemission, we show that the inelastic lifetime τ_{ee} of optically excited electrons of copper depends crucially on whether the electron is excited by an intraband or an interband transition. These results indicate clearly that τ_{ee} of photoexcited electrons is determined not only by the available phase space for the inelastic scattering process, but also depends on the initial state of the excited electron.

Keywords: Copper; Electron density, excitation spectra calculations; Low index single crystal surfaces; Metallic surfaces; Photoelectron emission; Visible and ultraviolet photoelectron spectroscopy

1. Introduction

Through the technique of time-resolved two photon photoemission (TR-2PPE), it has recently become possible to investigate the inelastic lifetime τ_{ee} of single electronic states of metals below the vacuum energy [1-4]. In general, the energetic relaxation of a single excited electron is dominated by ultrafast (a few fs) scattering with a "cold" electron of the Fermi sphere, creating an additional electron-hole pair. By means of many electron-electron collisions, the entire electron gas will finally relax to a new thermalized state. The theoretical analysis of this relaxation at a given energy $\epsilon = (E_i - E_F)$ above the Fermi energy is usually based on the Landau theory of Fermi liquids, which treats the excitation as a quasiparticle. Using the approach taken by Quinn [5], which does not

include d-band effects and exchange effects, the lifetime τ_{ee} of a quasiparticle located near the Fermi surface is given by

$$\tau_{ee} = \alpha(r_s, E_F) \frac{1}{(E_i - E_F)^2},$$

where α is a prefactor which depends on the dimensionless parameter r_s/a_0 for the free electron sphere and the material-dependent Fermi energy E_F . The dependence of the lifetime on $1/(E_i - E_F)^2$ appears as a consequence of the Pauli-principle restrictions on the number of available unoccupied states for both electrons involved in a scattering process.

In view of the recent activity in this area, the question arises as to whether the inelastic scattering process of the excited electrons can really be considered independent of its creation process. Filled d-band materials, such as the noble metals, provide an ideal system for studying the relaxation

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dynamics of hot electrons, which are excited by intraband ($sp \rightarrow sp$) and interband ($d \rightarrow sp$) transitions. For electrons involved in transitions near the Fermi surface, just one band will be involved in the transition process. Only for higher energy transitions (Au and Cu: $h\nu > 2.2$ eV, Ag: $h\nu > 4$ eV) do interband events become important.

Here we present a time-resolved two photon photoemission study of the inelastic lifetime τ_{∞} of photoexcited electrons in an energy range above and below the interband-transition threshold. The message of this paper is that the lifetime of the excited electron decreases rapidly as soon as excited d-electrons dominate the spectrum ($\epsilon < \epsilon_{\text{thr}}$).

2. Experimental

The experimental pump-probe set-up is very similar to that reported in Refs. [2,4]. Two equally intense, collinear, orthogonal polarized laser pulses with an adjustable delay interact with the metal surface. The combined, time-averaged photocurrent at a fixed kinetic energy is measured as a function of the delay between the two UV laser pulses (two-pulse correlation experiment). Due to a precise measurement of the delay Δt between the two pulses, this technique allows us to analyze lifetimes which are considerably shorter than the laser pulse duration.

The sample was mounted in a UHV chamber equipped with a cylindrical sector analyzer. The orientation of the Cu(111) sample was 45° relative to the laser beam and normal to the entrance axis of the energy analyzer. Before the experiments, the sample surface was carefully cleaned by argon-ion sputtering and annealing cycles.

The time-resolved 2PPE experiments were performed with a femtosecond mode-locked Ti:sapphire laser. The linearly polarized output is frequency-doubled in a 0.2 mm thick beta barium borate (BBO) crystal to produce UV pulses at $h\nu = 3\text{--}3.4$ eV with a duration of 40 fs. To extend the energy spectrum of the sample to lower energies ($\epsilon < \epsilon_{\text{min}} = \Phi - h\nu \approx 1.6$ eV for Cu), we reduced its work function by depositing a small amount of Cs on the surface (less than 0.1 ML). Within our

time resolution we did not observe a difference in the lifetime measurement between a clean Cu sample and a Cs/Cu sample in the overlapping energy region $1.6 \text{ eV} < (E_i - E_F) < 3.3 \text{ eV}$ using cross-polarized pulses.

3. Results and discussion

A typical two-photon photoemission spectrum for normal emission of a Cu(111) surface, taken with cross-polarized pulses at zero delay (filled circles), is shown in Fig. 1. The spectrum exhibits two well-defined features at $E_{\text{kin}} = 0.6$ eV and $E_{\text{kin}} = 2.15$ eV. The peak at $E_{\text{kin}} = 0.6$ eV is attributed to 2PPE from the top peak of the filled Cu d-bands, and is in agreement with band-structure calculations and measurements [6]. The peak at $E_{\text{kin}} = 2.15$ eV originated from a unoccupied alkali valence state, in full agreement with Fischer et al. [7]. In accordance with the σ -like symmetry of this

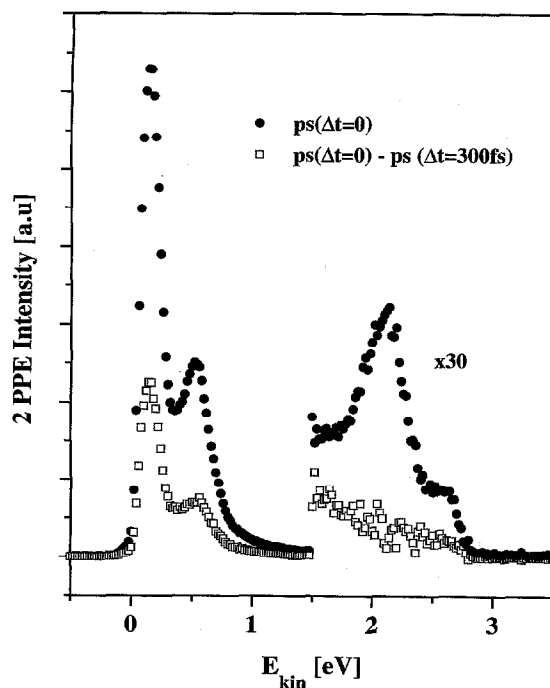


Fig. 1. Two-photon photoemission spectrum of the Cu(111) surface recorded by cross-polarised pulses at zero delay (filled circles) and corrected for the background contribution of each beam alone (open squares).

unoccupied alkali state, no emission feature was observed at this energy for s-polarized light. Therefore, this unoccupied alkali valence state contributes to the background signal only due to 2PPE from the p-beam, and does not contribute to the time-resolved 2PPE signal using cross-polarized pulses (see open squares in Fig. 1).

Fig. 2a shows the extracted lifetime τ_{ee} as a function of the intermediate state energy for a Cu(111) surface, using a photon energy of $h\nu = 3.3$ eV. The solid line represents the respective p-polarized spectrum, back-calculated to the intermediate state $\epsilon = (E_i - E_F) = \Phi + E_{kin} - h\nu$. As expected, the lifetime increases as the excited-state energy decreases. However, at an intermediate state energy $\epsilon = 1.1$ eV, where the spectrum becomes

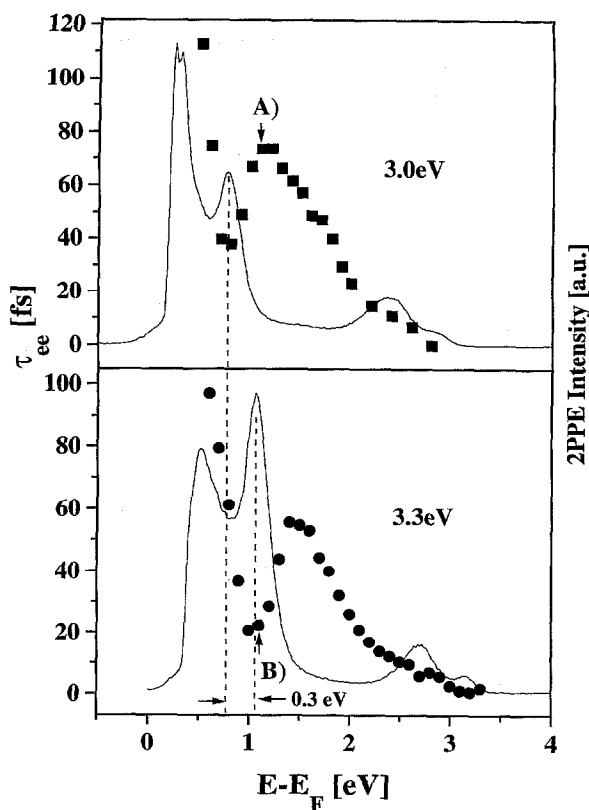


Fig. 2. Extracted lifetime τ_{ee} as a function of the intermediate state energy $\epsilon = (E_i - E_F)$ for a Cu(111) surface, using a photon energy of (a) $h\nu = 3.3$ eV and (b) $h\nu = 3.0$ eV. The solid line represents the respective p-polarized spectrum, back-calculated to the intermediate state.

dominated by excited 3d electrons, the lifetime τ_{ee} decreases from 60 to 20 fs before it increases again. By changing the photon energy to $h\nu = 3.0$ eV (see Fig. 2b), the peak in the intermediate spectrum ($E - E_F = \Phi + E_{kin} - h\nu$) shifts with $\Delta E = \Delta h\nu$, as expected for occupied electronic states. The dip in the measured lifetime moves with the same energy difference.

According to the Fermi liquid theory, the inelastic lifetime τ_{ee} of an optically excited electron is determined by the available phase space and is hence independent of the photon energy used. That this is the case can be seen in the energy region 1.5 eV $< (E_i - E_F) < 3.3$ eV. At lower energies, however, the lifetime depends critically on the photon energy used. These results clearly indicate that the inelastic lifetime τ_{ee} of photoexcited electrons is determined not only by the available phase space for the inelastic scattering process (points A and B in Fig. 2 represent the lifetime of the same excited electronic state), but also depends on the initial state of the excited electron. Using 3.0 eV photons (point A) only intraband transitions into the intermediate state 1.1 eV above E_F are possible according to the band structure. Using 3.3 eV photons (point B), however, the intermediate state at 1.1 eV above E_F is filled for the most part by interband transition from the d-band to the unoccupied sp band. Physically, one might understand this behavior as events where the mean free path picture, in which scattering of the photoexcited electron is treated independently of its birth process, has broken down. Furthermore, this dip in τ_{ee} was also reproducibly observed in measurements of polycrystalline Cu and Au samples.

The increasing number of carriers in the energy region where d-electrons can be excited may decrease the lifetime due to enhanced carrier-carrier scattering. However, this would influence the lifetime of all excited electrons and not just of the electron in the energy range of the dip. Furthermore, we changed the laser intensity by an order of magnitude and did not observe any differences in τ_{ee} versus $(E_i - E_F)$. This proves the absence of a lifetime influence due to an increased number of carriers by exciting d-electrons.

The observed difference in the lifetime of an excited electron between interband and intraband

transitions might be explained qualitatively as follows. The sp-band of Cu shows some similarity to a nearly free-electron band, in contrast to the more localized d-bands which have a tight-binding character. As illustrated in Fig. 3, direct (vertical) optical intraband excitations are, in general, not possible. Transition from an occupied sp state to an unoccupied sp state from the same band are possible only by momentum contribution due to a scattering process on defects, impurities, or phonons. All these processes lead to electron–hole dephasing, markedly reducing the chance that the electron may recombine with its own hole. Hence, for an intraband (k -nonconserving) transition the electron and its own hole have a different momentum and phase, and therefore no direct backfilling (without momentum contribution from a second process) of its own hole is possible. On the other hand, vertical transitions are possible for intraband transitions, as seen in Fig. 3. There is an increased chance that the excited electron will fill its own hole. Hence, there is an additional strong decay channel for vertical transitions, for which the wave

vectors k of the electron and hole match each other; this is the recombination of the excited electron with its own hole. Due to the fact that there is no satisfactory theoretical description at hand to treat the optical excitation process and many-body effects in the decay of the photoexcited electrons on a fs time-scale, this explanation may not be an exclusive one.

4. Conclusion

We have presented experimental evidence that the inelastic lifetime τ_{e} and hence the mean free path of photoexcited electrons is not only determined by the available phase space for an electron–electron process. The dynamics of an photoexcited electron depend critically on the history of the generation process of the excited electron, i.e. whether the initial state of the electron originates from a d- or sp-band.

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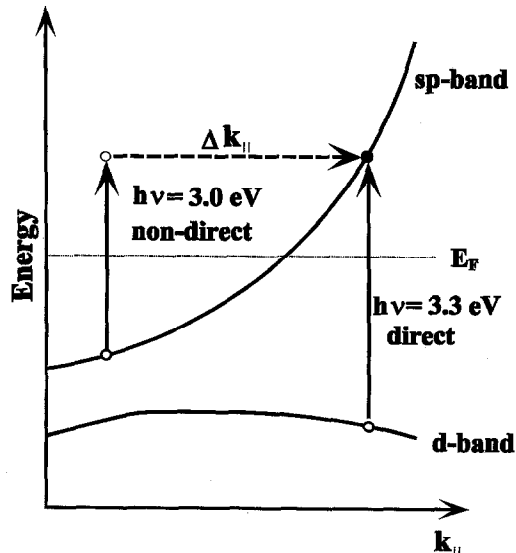


Fig. 3. Schematic diagram of indirect (k -nonconserving) intraband and direct (k -conserving) interband transitions.