Hole Decoherence of *d* Bands in Copper

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d-band hole decoherence times in copper are measured with energy and momentum resolution for the Cs/Cu(100) surface at 33–300 K by the interferometric time-resolved two-photon photoemission technique. At the top of the *d* bands (X_5 point) at 33 K the measured hole decoherence time of $T_2 = 34.5 \pm 1.5$ fs has contributions from the population decay due to Auger recombination ($\tau_{hh} = 24 \pm 3$ fs), and momentum scattering due to the hole-phonon interaction with a mass enhancement factor $\lambda = 0.20 \pm 0.01$. Rapid decrease of T_2 with binding energy below the X_5 point suggests a larger cross section for $3d$-$3d$, as compared to $3d$-$4sp$ band scattering.

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Angle-resolved photoemission (PE) spectroscopy is the premier method for mapping of the quasiparticle bands [1,2], and at highest resolution it also gives their homogeneous widths [3]. Although band structures of most metals are well known from experiment and theory, the carrier energy and momentum relaxation processes that determine the PE linewidths are just entering a stage of intensive study. PE spectral lineshapes provide information on the relaxation of the quantum mechanical phase of the optically excited *e*-*h* pair due to the carrier-carrier, carrier-phonon, and other complex interactions. Spectral functions derived from the lineshapes are the basis for discussing the quasiparticle dynamics in a variety of complex systems such as metallic nanostructures and high-temperature superconductors [4]. Copper, one of the most extensively studied materials by PE spectroscopy and theory, provides a model for other noble and transition metals [1,2,5,6]. By contrast to other $3d$ metals, copper offers a well resolved spectrum of fully occupied *d* bands, between -2 to -5 eV below E_F, which are the subject of numerous studies of the Auger recombination (*h*-*h* scattering) [2,5,7,8]. Nevertheless, our experimental and theoretical understanding of Auger recombination for the itinerant bands of $3d$ metals is still rudimentary compared to more extensively studied core holes [9]. A fundamental understanding of the carrier-carrier and carrier-phonon interactions in $3d$ metals is of great importance, because the same interactions that induce phase decoherence also play a key role in, for instance, magnetic recording and catalysis.

The following conclusions can be drawn from extensive studies of the *d*-band linewidths in copper. The narrowest linewidths in a range of 45–200 meV are observed at the top of the *d* bands [2,5,7,8]. As the binding energy increases, the reported widths increase with either a linear [$\Gamma \approx (E - E_F)$ [5]] or quadratic [$\Gamma \approx (E - E_F)^2$ [2,7,8]] energy scaling. The former is consistent with measurements on other materials [8,10,11], while the latter with the Fermi liquid theory (FLT) for a free-electron gas. However, neither scaling can be derived from the joint density of initial and final states that determines the phase space for *h*-*h* scattering [12]. From PE measurements it is difficult to deduce the true Auger recombination rates because, in addition to the carrier lifetime, Γ can have contributions from inhomogeneous sources, and *quasielastic* hole-phonon (*h*-ϕ) momentum scattering, which is a substantial source of decoherence in metals even at 0 K. Because of these unknown contributions, the linewidth analyses overestimate the Auger recombination rates in copper, and no theoretical values have been reported.

Time-resolved two-photon photoemission, an alternative method for studying the carrier phase and energy relaxation directly in the time domain, has an advantage over linewidth analysis in that it is easier to distinguish the elastic and inelastic carrier scattering processes [13–17]. Such studies have been performed thus far only on surface states where carriers are partially delocalized in the vacuum, and the Coulomb interactions with the bulk carriers and the lattice are relatively weak. Time-domain techniques also make possible the coherent control of the carrier dynamics provided that the decoherence rates are sufficiently slow and characterized with respect to the band structure [15]. In this Letter, the energy and temperature dependence of the *d*-band decoherence in copper is studied in the time domain by the interferometric time-resolved two-photon photoemission (ITR-2PP). The measured decoherence time of 34.5 ± 1.5 fs at the top of the *d* bands at 33 K has a dominant contribution from the Auger recombination with $\tau_{hh} = 24 \pm 3$ fs. This sets a new benchmark time for the Auger recombination in a $3d$ metal for comparison with theory and the modeling of the carrier relaxation dynamics, and establishes the limits for the coherent control of bulk carriers.

Details of the ITR-2PP experiment and data analysis are described in Ref. [13]. Briefly, frequency-doubled light from a Ti:sapphire laser ($h\nu = 3.08$ eV; 13 fs width of the pulse intensity envelope) is split into equal pump and probe pulses in a Mach-Zehnder interferometer (MZI). The difference between the path lengths of the two arms of the MZI, and therefore, the pump-probe delay, is scanned under feedback control by ± 150 fs with an accuracy and reproducibility of <50 as [13–15]. The pulse pair is focused to a spot of ~ 80 μm on the Cu(100) surface within

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an ultrahigh vacuum chamber (pressure $<5 \times 10^{-11}$ torr). The photoemission current is induced with s- or p-polarized light incident at 30° from the surface normal, and measured for $k_{\|} = 0$ in an energy resolved fashion with a hemispherical electron energy analyzer (5° angular and <28 meV energy resolution). The limiting spectral resolution of ~75 meV for the two-photon photoemission (2PP) is due mainly to the bandwidth of the 13 fs laser pulses. Depositing 0.10 monolayer (ML) of Cs [1 ML corresponds to a (2×2) Cs/Cu(100) structure] from a SAES getter source onto the Cu(100) surface reduces the work function Φ by ~1 eV, allowing the observation of the d bands below −2 eV [18]. The sample temperature is controlled between 33–300 K with a closed-cycle He refrigerator/heater combination.

Figure 1 shows 2PP spectra of Cs/Cu(100) with p- and s-polarized excitation including the relevant band structure for $k_{\|} = 0$ [12], which indicates the possible initial E_0, intermediate E_1, and final states E_2 in the 2PP process. With p-polarized excitation the d-band features consist of an intense peak at $E_0 = -2.23$ eV and a shoulder at $E_0 = -2.01$ eV [19]. With s polarization the main peak has a 13 meV larger binding energy and ~30 meV narrower width, while the shoulder is missing. The shoulder consists of two overlapping peaks as deduced from a difference spectrum between the p- and s-polarized spectra. The p-polarized spectrum in Fig. 1 is fit with *three* Gaussian peaks at −2.24, −2.14, and −2.01 eV having relative intensities of ~5:1:1, and Gaussian widths of 105, 83, and 80 meV, respectively. PE spectra and theory predict three bands at ~ − 2 eV: the Δ_5, which is split at the X_5 point [top of the d bands (see inset of Fig. 1)] by 0.10–0.14 eV into X_{7^+} and X_{6^+} due to the spin-orbit (s-o) interaction; and the Δ_2 band [1,6]. From energetic considerations, the shoulder can be assigned only to the s-o components of X_5. The main peak energy is consistent with the X_2 point; however, the $\Delta_2 \rightarrow \Delta_1$ transition is symmetry forbidden. More likely, the main peak is due to the $\Delta_5 \rightarrow \Delta_1$ transition, which provides the maximum enhancement of 2PP at 3.61 eV [20]. The intensity of the d bands in the 2PP spectrum of Cu(100) is 9 times larger than for the nearly isoenergetic peaks of Cu(111) and Cu(110) probably because of enhancement by one-photon resonance involving either the Δ_1 band or the surface resonance at 1.1 eV, as indicated in Fig. 1 [21].

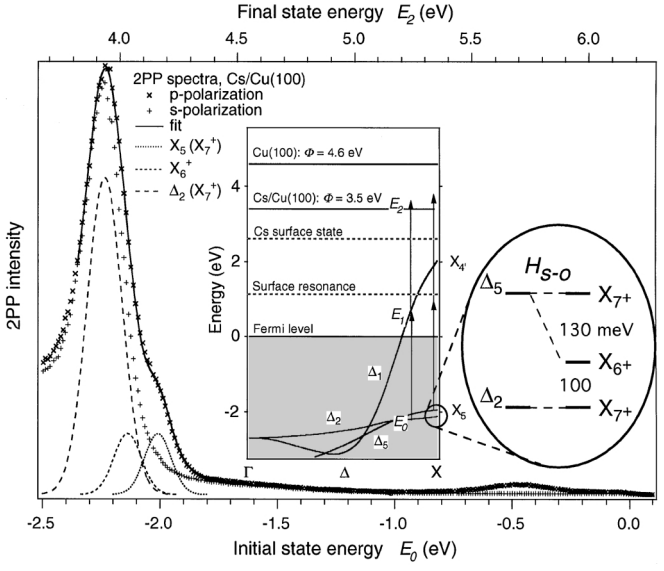

FIG. 1. s- and p-polarized 2PP spectra of Cs/Cu(100), and decomposition of the p-polarized spectrum into three bands. The inset shows the band structure of Cs/Cu(100) for $k_{\|} = 0$ along with a detail near the X_5 point.

Figure 2(a) shows a representative interferometric two-pulse correlation (I2PC) where the 2PP current is recorded for $k_{\|} = 0$ and $E_0 = -2.01$ eV as a function of the pump-probe delay. The I2PC scans measure the phase relaxation of coherence among the E_0, E_1, and E_2 levels through elastic and inelastic carrier scattering, as well as the population decay of E_1 [13,14]. The rapidly oscillating signal

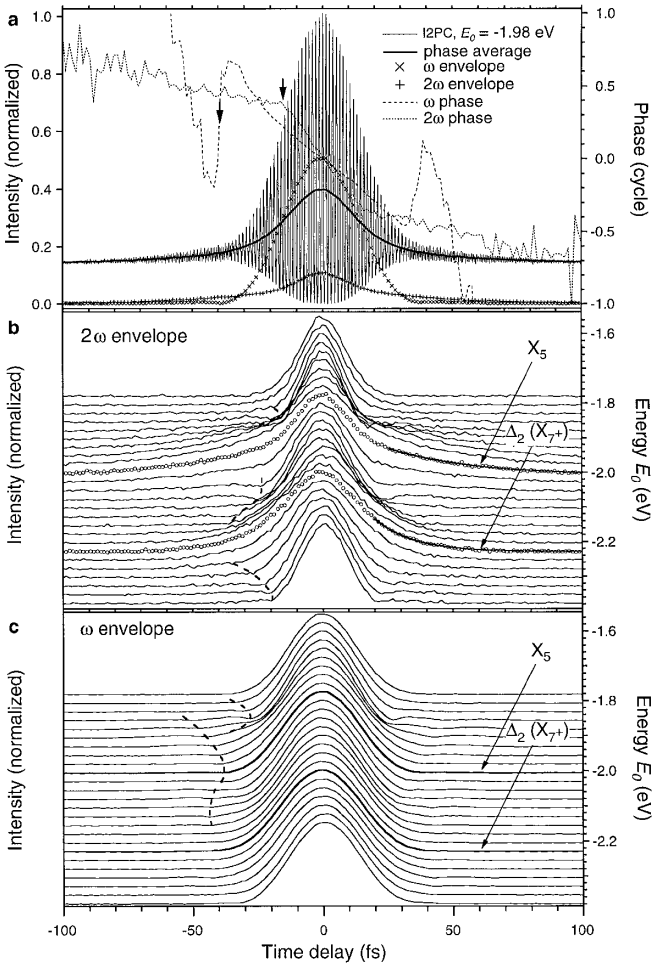

FIG. 2. (a) A representative I2PC scan measured at $E_0 = -2.01$ eV, and its decomposition into phase and envelope components. Arrows indicate discontinuities in phase of the coherent oscillations; (b) 2ω envelopes for $E_0 = -2.38$ to -1.78 eV in 0.025 eV intervals (right axis gives E_0 for each measurement). Single exponential fits are shown for the X_5 point and d-band intensity maximum. Dashed lines guide the eye to the nodes in the coherent beats; (c) ω envelopes.

at the excitation frequency ω and its second harmonic 2ω reflects both the optical interference between the pump and probe pulses in the MZI and quantum interference between the pump and probe induced polarization waves in the sample. Although free induction decay of coherent polarization, i.e., reflection from a metal surface, is nearly instantaneous due to large ($\sim h\nu$, or E_F) inhomogeneous broadening, with ITR-2PP it is possible to measure the energy and momentum resolved polarization decay rates since the coherent signal is monitored within a smaller energy window than the homogeneous bandwidth [19]. The I2PC data are analyzed by decomposing the signal into its phase average and the envelopes of ω and 2ω oscillations [13]. Figures 2(b) and 2(c) show the 2ω and ω envelopes for different values E_0 across the d-band feature. The reduced data are fit to a convolution of the autocorrelation of the laser pulse with a single exponential decay to determine the population decay time T_1 for E_1 from the phase averaged signal, and decoherence times T_2^{ω} and $T_2^{2\omega}$ of linear and nonlinear polarizations from the ω and 2ω envelopes, respectively [13]. Furthermore, the ω and 2ω oscillations are compared with the optical interferogram of the pump and probe pulses, which provides an internal clock with a 1.34 fs period corresponding to one cycle of the excitation light, to determine the evolution of the phase of the polarization oscillations with respect to the driving field. Phase plots such as in Fig. 2(a) provide information on the beats that modulate the envelopes for some energies.

The actual evaluation of $T_2^{2\omega}$ and T_2^{ω} is complicated by the presence of coherent beats in the ω and 2ω envelopes, which probably arise from both (i) quantum beating due to the coherent excitation of the three d bands and (ii) polarization beating that results from interference between the polarizations induced at the driving frequencies ω and 2ω and those defined by transitions between the real states $E_0 \rightarrow E_1$, $E_1 \rightarrow E_2$, and $E_0 \rightarrow E_2$ that are excited in the metal. According to the energy splittings in Fig. 1, quantum beats should have well defined *periods* of 18, 32, and 42 fs, and only the *amplitudes* of different eigenstates should depend on the observation energy. By contrast, the polarization beats depend on the observation energy since this defines the difference frequencies between $E_2 - E_1$ and ω, and $E_2 - E_0$ and 2ω [22]. Furthermore, the d bands are coupled through the Coulomb interaction, and therefore the beats probably also contain additional information on the many-body e-e correlations that underlie the decoherence process. Since the beating in the ω and 2ω envelopes depends on E_2, as can be seen in Fig. 2, it is likely that both the quantum and polarization beats contribute to the nonexponential decay kinetics. To derive the experimental values of $T_2^{2\omega}$ and T_2^{ω} in Fig. 3, the envelopes are fit with single exponential decays; this gives excellent fits at the X_5 point and the d-band intensity maximum, but it cannot represent adequately the complex interference effects. The longest $T_2^{2\omega}$ at 33 K of 34.5 $\pm$ 1.5 fs corresponds to a linewidth of 38.3 meV and is comparable to the minimum PE linewidth of 45 meV at 130 K [2,23].

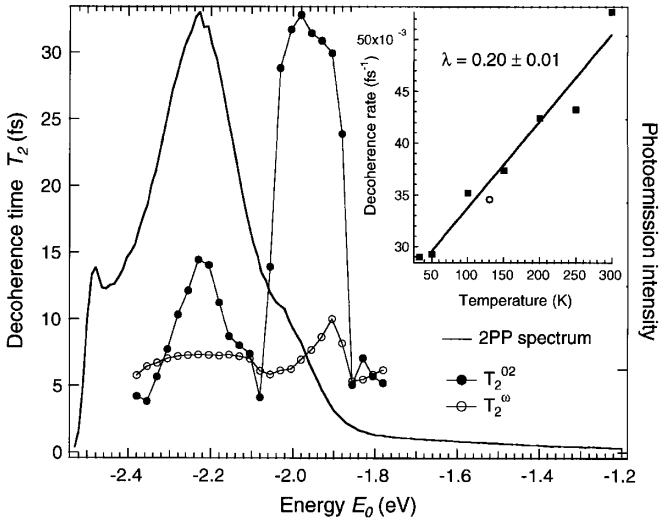

FIG. 3. The experimental values for exponential decay times of the linear T_2^{ω} and nonlinear $T_2^{2\omega}$ polarizations. $T_2^{2\omega}$ plot shows a pronounced maximum in the hole decoherence time at the X_5 point. Inset shows the temperature dependence of $(T_2^{2\omega})^{-1}$ at $E_0 = -2.01$ eV (■) along with $(T_2^{2\omega})^{-1}$ from the PE linewidth analysis (○) [23].

The remaining part of this Letter will focus on the decoherence rates of the nonlinear polarization $(T_2^{2\omega})^{-1}$, which can be written as a sum of scattering rates of the hole and photoelectron that are generated by two-photon excitation $(T_2^{2\omega})^{-1} = \Gamma_h + \Gamma_e$. The X projected gap extends between 2 and 8 eV [1,6], and therefore $k_{\parallel}$ conserving transitions at $k_{\parallel} = 0$ for Cu(100) can excite electrons only to the evanescent band gap states, i.e., free-electron waves in the vacuum with an exponentially damped probability in the bulk [1,2]. A lower limit for $\Gamma_e^{-1} = 2$ ps at $\sim$4.6 eV, which is estimated from the lifetimes of high ($n \geq 6$) image potential states on the Cu(100) surface [17], indicates that the Γ_e contribution to $(T_2^{2\omega})^{-1}$ can be neglected, and, thus, $(T_2^{2\omega})^{-1} \approx \Gamma_h$. Although Γ_h also contributes to the decay of the linear polarization, the interpretation of T_2^{ω} is more complicated because it has contributions from the phase relaxation of electrons at E_1.

The decoherence rate of d holes can be decomposed into contributions from h-h and hole-phonon (h-ϕ), and hole-defect (h-d) scattering according to $(T_2^{2\omega})^{-1} = \Gamma_{h\phi}(T) + \Gamma_{hh} + \Gamma_{hd}$ [3,24]. Although h-d scattering in clean metals is important only at much lower temperatures and energies, Cs atoms contribute 2.5% surface impurity concentration. However, measurements with different Cs coverages, as well as for $k_{\parallel} \neq 0$, suggest that the impurity scattering does not contribute significantly to $(T_2^{2\omega})^{-1}$. Although the broadening of surface state linewidths by alkali atom adsorption is significant [24], the effect on the d bands should be much smaller since the bulk holes are screened from surface defects and have smaller group velocities. The effect of h-ϕ scattering can be deduced from the temperature dependence of $(T_2^{2\omega})^{-1}$ at the X_5 point, which is shown in the inset of Fig. 3. According

to the Debye theory, the temperature dependence of h-ϕ scattering is given by $\Gamma_{h\phi} \approx 2\pi\lambda k_B T$, where λ is the e-ϕ mass enhancement factor [3,25]. The linear fit of $(T_2^{2\omega})^{-1}$ vs temperature gives $\lambda = 0.20 \pm 0.01$, which is the same as for the h-ϕ scattering at the Fermi surface in the Γ-X direction [25]. The Auger recombination rate of $\Gamma_{hh} = 0.021$ fs^{-1}, corresponding to a 24 $\pm$ 3 fs lifetime for holes at X_5 (X_{7^+}), is determined by subtracting the h-ϕ contribution from $(T_2^{2\omega})^{-1}$. This value should be considered as a lower limit since the defect scattering may contribute to a small extent and $T_2^{2\omega}$ measurements are close to the instrument coherence time of >47 fs.

The measured value of $\tau_{h\text{-}h}$ at X_5 is considerably longer than the literature values from FLT and PE linewidth analysis. Although the frequency and time-domain measurements are consistent, the conclusions regarding the Auger recombination are significantly different because h-ϕ contribution has not been considered in the PE linewidth analysis. The energy dependence of the PE linewidth, $\Gamma_{hh} = (0.012\ \text{eV}^{-1})(E - E_F)^2 + 0.02$ eV [2,7,8], gives the Auger recombination rate at the X_5 point of 9.7 fs, which is ~2.5 times faster than reported in this Letter. Furthermore, the putative $\tau_{hh}^{-1} = (E - E_F)^{-2}$ scaling implies a ratio of τ_{hh} of 1.2 for $E = -2.01$ and 2.23 eV, rather than the observed 1.5 for the X_5 (X_{7^+}) point and the d-band intensity maximum [obtained by subtracting $\Gamma_{h\phi}$, which is essentially independent of binding energy [3], from the $(T_2^{2\omega})^{-1}$ values at each energy]. More rapid increase in the Γ_{hh} than predicted by the FLT energy scaling shows that the free-electron gas model does not describe the Auger decay of d holes [13,21]. Significantly faster h-h scattering rates for bands below X_5 (X_{7^+}) may arise from additional phase space due to the relaxation within the d bands. In addition, the cross sections also may be larger for d-d rather than for d-sp scattering due to better overlap in the M shell, where the electrons are more tightly bound than for the free-electron-like N shell [9,13].

In summary, decoherence of d-band holes in Cu(100) due to h-h and h-ϕ scattering is measured directly by the interferometric time-resolved two-photon photoemission technique. Coherent polarization induced by two-photon excitation of the spin-orbit split X_5 and nearby Δ_5 bands decays in a complex manner involving coherent beats. The temperature dependence of the decoherence rates is used to determine the hole lifetime of 24 $\pm$ 3 fs due to Auger recombination at the top of the d bands and the e-ϕ mass enhancement factor $\lambda = 0.20 \pm 0.01$. This is the first benchmark measurement for comparing the experimental Auger recombination rates of the 3d valence bands with theory, and it shows that both h-h and h-ϕ scattering must be considered in the PE linewidth analysis. A dramatic increase in the h-h scattering rates between the X_5 point and Δ_5 band cannot be explained by the free-electron gas model, suggesting that both the phase space and the cross section for h-h scattering within the 3d bands are larger than for the 3d-4s Auger recombination. Since a significant amount of energy is deposited in long-lived d holes in excitation with >2 eV photons [13], Auger recombination must have an important role in hot-electron dynamics and surface photochemistry in copper [13,21,26]. Finally, the discovery of long decoherence times for the d bands of copper opens the possibility of coherent control of the electrical, magnetical, optical, and chemical properties of d-electron metals.

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