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Time-resolved two-photon photoemission from Cu(100): Energy dependence of electron relaxation

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A time-domain measurement of the relaxation time of photoexcited electrons as a function of excitation energy at a single-crystal Cu(100) surface has been made with time-resolved two-photon photoemission. The relaxation lifetime of the excited electrons is found to decrease rapidly with the amount of excitation energy above the Fermi level, and we compare the measured lifetimes with a calculation based on Fermi-liquid theory. The results reveal a qualitative agreement with the theory, and indicate that effects due to transport of the electrons away from the surface and into the bulk are important.

In this paper, we report our recent measurements of excited-state lifetimes of photoexcited hot electrons in single-crystal Cu(100) using time-resolved two-photon photoemission. This study is a direct measurement of the excited electron lifetime as a function of excitation energy in a single-crystal sample. The single-crystal sample minimizes possible effects from defects or impurities, which allows us to focus on the fundamental electron-electron interaction. An important difference between the work presented here and previous studies is that the laser-pulse energy was kept very low (<0.5 nJ/pulse). Therefore, less than one electron per laser pulse is emitted, which avoids any problems due to distortion of the photoelectron spectrum from space-charge effects, and transient thermal heating of the lattice is also avoided. We find that the excited electrons relax in qualitative agreement with Fermi-liquid theory over a limited energy range, limited at higher energy by our finite temporal resolution, and at lower energy by transport effects.

Time-resolved two-photon photoelectron spectroscopy studies of metal and semiconductor surfaces provide valuable information regarding the electronic environment by revealing dynamical information as well as the energetics of the system. Furthermore, the energetics and dynamics of the *unoccupied* states as well as the occupied states are provided by the fact that it is a two-photon process, which is sensitive to the density and lifetime of the intermediate (unoccupied) states.[1,2]

An important class of studies probes electron-lattice coupling in thin metal films where an intense laser pulse generates transient hot electrons.[1,3–7] Using the technique of transient thermoreflectivity and thermotransmissivity, several groups have investigated the electron-lattice and electron-electron coupling and found the electron relaxation time due to coupling with the lattice to be on the order of 1–3 ps,[3–5] and that the rate of electron transport in thin films is on the order of the Fermi velocity, 10 Å/fs.[4]

A more direct measure of the electron distribution is provided by two-photon photoemission since the energy of the photoemitted electrons is known precisely from their kinetic energy, the work function, and the photon energy used to emit them. There are several previous studies in which two-photon photoemission has been used to investigate the unoccupied states of clean metal and adsorbate-metal systems.[8–15] Recently, the full power of time-resolved photoemission spectroscopy has been used by Fann *et al.* to characterize the time scale of the formation of an electronic equilibrium as well as the concurrent and subsequent electron-lattice relaxation after laser heating of a thin polycrystalline gold film by an intense laser pulse.[1]

It is obvious that it will be impossible to determine the relaxation rate from frequency-domain measurements for the present case of excited electrons in a continuous band simply because no discrete spectral features exist. Even in cases where discrete features such as surface states do exist, the pitfalls of using linewidths to determine lifetimes have been clearly demonstrated in the case of a surface state of Cu(111), wherein the spectral width of the feature actually *increased* upon approaching the Fermi level.[16,17] Time-domain measurements are therefore required to determine the lifetime in the presence of mechanisms that broaden spectral features. Furthermore, time-domain measurements of image states on Ag(100) have demonstrated the ability to determine lifetimes that cannot be accurately measured otherwise due to limitations of instrumental resolution.[11,12]

Our experiment is designed to measure electron dynamics at metal surfaces. By using a low-pulse-energy and high-repetition-rate laser, as opposed to a low-repetition-rate and high-pulse-energy laser, we avoid ambiguities that might arise in a highly excited electron distribution or space-charge effects that can distort the measured photoelectron spectrum. We measure the relaxation of individual excited electronic states rather than the collective behavior of a transiently heated nonequilibrium distribution. This is an important dis-

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tinction because photoinduced surface chemistry employing conventional low-flux cw light sources such as arc lamps fall in the category of individually excited states.[18] Several examples of surface-desorption and surface-dissociation processes are believed to be driven by subvacuum-level excited electrons. Dynamical information about the excited electrons such as that presented here will provide additional constraints regarding the extent and duration of interaction between the adsorbate molecules and the excited electrons.

The laser system used in these studies consists of a self-mode-locked Ti:sapphire laser pumped by about 7.7 W from a cw Ar^+ laser producing about 9 nJ/pulse with a 50-fs pulse width at 82 MHz, with tunability from 750 to 850 nm. The second harmonic (2.92–3.31-eV photon energy) is generated without additional broadening by using a 250-μm-thick Beta Barium Borate (BBO) doubling crystal, which achieves roughly 10–15 % conversion efficiency, and a pair of external prisms for group-velocity dispersion compensation of the frequency-doubled pulses is employed.[19] Equal intensity pump and probe pulses are used.

The ultrahigh vacuum system uses standard techniques to achieve a base pressure of 1×10^{-10} torr. A clean and well-ordered surface is obtained by sputtering with argon ions and annealing at 700 °C. The Cu(100) sample is oriented at 45° relative to the laser beam. The sample is normal to the entrance axis of the energy analyzer, which is located 1.5 cm from the sample. A -3.0-V bias is applied to the sample to eliminate the effects of any stray electric fields. The applied bias voltage extends the range of **k** states being collected, but contributes less than 0.1-eV uncertainty to the energy resolution since the bias is small and copper exhibits nearly-free-electron behavior. The crystallographic [010] direction is horizontal (in the plane formed by the incident and reflected laser beam) when the azimuthal angle is 0°, and the azimuthal angle was held at 0° for the data presented here. As seen in Fig. 1(a), the energy of the intermediate state E_i above the Fermi energy E_F is given by $E_i-E_F=E_{\mathrm{KE}}+\Phi-h\nu$, where E_{KE} is the electron kinetic energy at the sample surface with the energy due to the bias voltage subtracted, Φ is the work function for copper (4.6 eV), and $h\nu$ is the photon energy (3.14 eV). The energy analyzer used is a 10-cm inner-radius hemispherical energy analyzer with roughly 1% relative resolution and 10° acceptance angle. A transmission energy of 20 V is used, which leads to roughly 200-meV resolution.

A schematic diagram of the two-photon photoemission process being measured is shown in Fig. 1(a), and a typical photoemission spectrum, taken with one of the two laser beams blocked, is shown in Fig. 1(b). The signal intensity varies quadratically with laser power, as expected for a two-photon process. The pump-probe experiments are typically carried out by monitoring the number of electrons at a given kinetic energy as a function of delay between the pump and probe pulses. Scans obtained when monitoring electrons at 4.8 and 3.2 eV of kinetic energy (3.26 and 1.66 eV above the Fermi level, respectively) are shown in the inset of Fig. 2(a), and the 2:1 intensity ratio at the peak relative to the baseline indicates a sequential (noncoherent) two-photon process. Figure 2(a) presents the full width at half maximum (FWHM) of the pump-probe scans as a function of photoelectron kinetic energy when using a photon energy of 3.14 eV. The FWHM decreases as the photoelectron kinetic energy increases, which is to say that the FWHM decreases as the energy of the intermediate state above the Fermi level increases. While the present study was carried out solely with a 3.14-eV photon energy, it was found in previous work utilizing different photon energies that the dynamics are independent of photon energy, and are determined by the position of the intermediate level E_i above the Fermi level E_F.[20] As we are not able to autocorrelate the frequency doubled output of the laser (380–420 nm) with a doubling crystal to determine its FWHM, we must rely on the pump-probe spectra at the highest electron kinetic energies to determine the pulse width. As seen in Fig. 2(a), the relaxation dynamics at high kinetic energy are faster than the laser pulse width since the FWHM decreases to a nearly constant value that is consistent with the 50-fs pulse width of the laser fundamental.

The effects of laser polarization were investigated. This study was conducted to determine if simultaneous two-photon processes or sequential two-photon processes involving intermediate levels dominate the signal. If the two-photon photoemission measured here were a *simultaneous* process, then there should be a dramatic difference in the pump-probe spectrum depending on the relative polarizations of the pump and probe pulses. We find that the pump-probe FWHM is independent of the relative polarization of the pump and probe beams. That is, the same type of behavior as shown in Fig. 2(a) is obtained for either parallel- or crossed-polarized laser pulses. The FWHM for the Gaussian functions fitted to scans taken with *P-P*, *P-S*, and *S-S* polarizations at 3.2-eV photoelectron kinetic energy are 98±5, 104±5, and 98±7 fs, respectively. This polarization independence of the dynamics indicates that the process we are measuring is a sequential two-photon process in which the electrons undergo elastic collisions between absorbing the two photons.

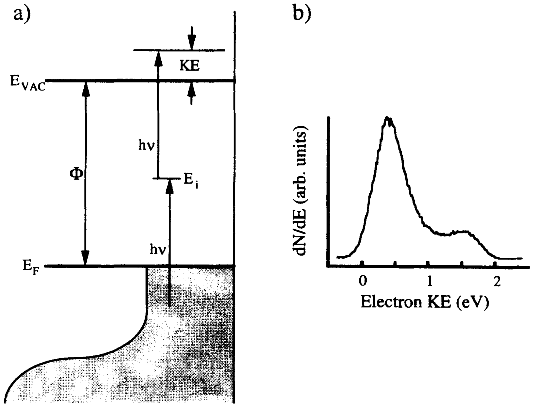

FIG. 1. Part (a) is a schematic representation of the two-photon process being measured. The shaded region indicates the density of occupied states. The photon energies used here access *s* electrons and the top of the *d* band. The work function Φ for Cu(100) is 4.6 eV, and the photon energy used in this study is 3.14 eV. Part (b) is the photoemission spectrum obtained with one beam blocked. The ~1.7-eV width of the spectrum (which is broadened to ~1.9 eV by the instrumental resolution of the energy analyzer) is obtained from the difference of the two-photon energy (6.3 eV) and the work function.

The dependence of the width of the pump-probe scans as a function of intermediate-state energy can be understood in terms of an energy-dependent relaxation time for the excited electrons. A semiquantitative description of the properties of electrons in metals with several eV of excitation energy above the Fermi level is obtained by treating the excitation as a quasiparticle,[21] and is referred to as Fermi-liquid theory. A quasiparticle refers to the excited electron as well as the distortion of surrounding particles brought on by the adiabatic interaction among particles.[21] A critical parameter in this treatment is r_s, the radius of the sphere (in units of the Bohr radius, a_0) containing the effective volume of an electron. Alternatively, r_s is the ratio of the average potential energy relative to the average kinetic energy of the Fermi liquid.[21] In metals, $1.8 \leq r_s \leq 5.6$, and for copper $r_s = 2.67$.[22] Fermi-liquid theory has successfully described electron relaxation in previous time-resolved measurements,[1] and it provides a fundamental description of electrons near the Fermi level. It is seen below, however, that some of the qualitative aspects of the measured energy dependence of the lifetimes are not in full agreement with the theory. Nonetheless, it provides an initial basis for comparison of the experimental results.

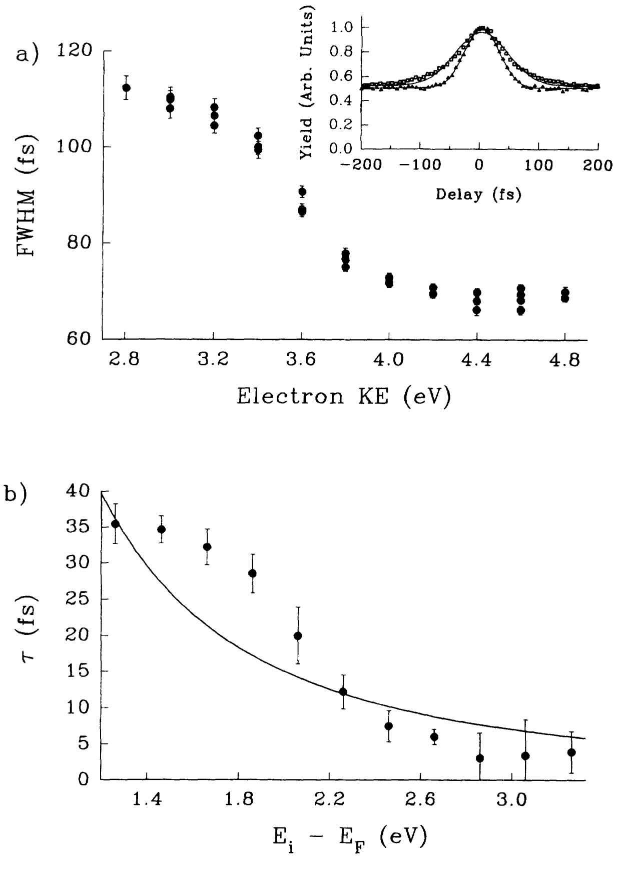

FIG. 2. Part (a) shows the FWHM of the pump-probe scans as a function of electron kinetic energy. The scans at different kinetic energies are not taken in order of increasing or decreasing kinetic energy to ensure that long-term drift does not affect the results. The error bars are one standard deviation uncertainty for the FWHM parameter obtained when fitting the scans to a Gaussian functional form. Typical pump-probe scans when monitoring electrons with 4.8- and 3.2-eV kinetic energy are indicated by filled triangles and open squares, respectively, in the inset. Part (b) is a comparison of calculated relaxation time constant τ with that deconvolved from the experimental data as a function of intermediate-state energy $E_i - E_F$, not kinetic energy of the emitted electron. The solid line is the result of Eq. (2) scaled by 2.45. The filled circles in part (b) are obtained by calculating the average of the deconvolved values of τ at each energy, and the error bars represent two standard deviations.

Using the approach taken by Quinn,[23] we can estimate the lifetime of the excited electrons by calculating the imaginary component of their energy, since the probability decays exponentially in time according to $e^{-t/\tau}$, with $\tau = \hbar/(2E_I)$. For low-energy excitations ($p/p_0 < 1.3$) the imaginary contribution to the energy is given by[23]

$$\begin{aligned} E_I(p) \approx {} & (e^2/2a_0)[\pi^{1/2}/32(\alpha r_s)^{3/2}][\tan^{-1}(\pi/\alpha r_s)^{1/2} \\ & + (\alpha r_s/\pi)^{1/2}/(1+\alpha r_s/\pi)][(p/p_0)^2 - 1]^2/(p/p_0), \end{aligned} \tag{1}$$

where $\alpha = [4/(9\pi)]^{1/3}$, p is the momentum of the excited electron, and p_0 is the momentum of the electrons at the Fermi level. Equation (1) can be evaluated with $r_s = 2.67$ and $e^2/(2a_0) = 13.6058$ eV to yield

$$\begin{aligned} E_I(p) &\approx 0.66[(E_i - E_F)/E_F]^2 \text{ eV}, \\ \tau &\approx 0.49[E_F/(E_i - E_F)]^2 \text{ fs}, \end{aligned} \tag{2}$$

where τ is the predicted lifetime, and p/p_0 in the denominator of Eq. (1) has been set equal to 1 since this treatment is only semiquantitative. The Fermi energy for copper, E_F, is 7.0 eV.[22]

In order to compare the experimental results with Eq. (2), it is necessary to deconvolve the exponential component of the measured pump-probe scans from the underlying Gaussian contribution due to the autocorrelation of the laser pulse. First, the FWHM of the autocorrelation was obtained by averaging together the FWHM of the Gaussian fits of the nine pump-probe scans obtained between 4.4 and 4.8 eV. Then a nonlinear least-squares-fitting routine was used to deconvolve the exponential component of the pump-probe scans from this underlying instrument-response function. The most important aspect of Fig. 2(b) is the observed trend in lifetime vs energy; therefore, the difficulty in extracting time constants that are less than $\frac{1}{3}$ the pulse width (which would place a 16-fs lower limit on τ) does not adversely affect our analysis, since it is not the actual value of τ, but rather the trend that is important. These experimentally determined decays can then be compared to the results of Fermi-liquid theory. The solid line in Fig. 2(b) corresponds to the predicted lifetimes obtained from Eq. (2) after being scaled by a factor of 2.45. This comparison shows that the predicted lifetimes are reasonably close to the observations, but the energy dependence of the relaxation shows a systematic deviation.

There are a number of possible explanations for the observed discrepancy from Fermi-liquid theory. First, for real metals where $r_s > 1$, Fermi-liquid theory only provides a qualitative description. There are also two other factors that affect the measured dynamics that are not accounted for in Fermi-liquid theory. One is that the measured photoemission yield will decrease if the excited electrons move out of the region probed by the laser on a time scale faster than their relaxation time. At 395 nm, the light penetrates roughly 150

Å into the metal; therefore, electrons that have a chance to move that distance have a much lower probability of being measured, even though they are still excited. We are currently investigating further the issue of transport, both experimentally and theoretically. The other factor contributing to the disagreement of the measured lifetimes and those calculated from Fermi-liquid theory arises from the fact that only the $4s^1$ valence electrons are included in the calculation, and the $3d^{10}$ electrons that are 1.5–2.0 eV below the Fermi level are neglected. A treatment of the electron dynamics that includes the full band structure of copper will be necessary in order to make a quantitative comparison with the measured lifetimes.

Finally, a comparison with the related studies of Fann *et al.*[1] is in order. This earlier, pioneering work utilized a UV probe pulse to monitor the evolution and decay of a transiently heated electron distribution generated by an intense pump pulse in a polycrystalline, 300-Å-thick gold sample via photoemission. They modeled their results as a process in which the nascent (nonthermal) electron distribution thermalized and allowed the thermalized electron distribution to couple with the lattice. They found that Fermi-liquid theory qualitatively described (within a factor of 2.5) the relaxation of the nascent electron distribution to one with an elevated temperature. Thus, an emerging trend from these studies is that the relaxation time calculated from Fermi-liquid theory is somewhat too small, but the fact that both studies obtain 2.5 as the scale factor must be considered fortuitous.

There are two substantial differences between this paper and Ref. 1. First, this paper employs a single-crystal sample, whereas that in Ref. 1 is polycrystalline. It is known that the electron dynamics are different in single-crystal and polycrystalline thin films[3] due to scattering from grain boundaries, and experiments performed with polycrystalline samples have an additional, uncharacterized, relaxation mechanism. The second, and more important, difference is that the present paper utilizes very-low-energy pulses, ~ 100-nJ/cm^2 absorbed fluence, whereas the absorbed fluence is as high as ~ 300 μJ/cm^2 in Ref. 1. Therefore, in Ref. 1, the electronic temperature reaches peak values of roughly 1500 K, and electron-phonon coupling must be considered in addition to electron-electron scattering. That is, the electron dynamics extracted from their model will depend on the parameter chosen for the electron-phonon coupling. Our experiment, on the other hand, has very low excitation levels, and the electronic temperature is not affected. At short times, on the order of 10–20 fs, before transport effects are significant, the measured relaxation time is only due to electron-electron scattering mechanisms. Therefore, a measure of the relaxation dynamics is obtained without having to invoke a model. While we do compare the measured dynamics with the results of Fermi-liquid theory, the actual measurement of the dynamics is independent of any model. The work in Ref. 1 and this paper are complementary to each other in many ways, and by considering the results of several experiments, a full description of electron relaxation dynamics will be obtained.

The results presented here demonstrate the feasibility of studying the relaxation of single electrons in metals directly in the time domain. It is seen that while Fermi-liquid theory is in qualitative agreement with these results, a more rigorous treatment will be necessary for quantitative comparisons since r_s for real metals is not within the range in which the random-phase approximation is expected to hold rigorously, and it will also be necessary to include the full band structure. Future work will address dynamical issues related to substrate-adsorbate hot electron transfer in the presence of the competing pathways of relaxation and transport into the bulk. Finally, the power of studies based on time-resolved laser spectroscopy is underscored by the statement made by Pines and Nozières:[21] "... it [Landau's theory of quantum liquids] uses (and provides) far more information than any experiment will ever sample. For example, one never detects experimentally *one* quasiparticle; put another way, one never *measures* the quasiparticle distribution δn_p. What is observed experimentally is always an *average* property of the system, its charge, current, magnetization, etc." Clearly, experimental technology has made significant and unforeseen advances during the last 30 years, as it is now possible to directly measure the behavior of the quasiparticle distribution.

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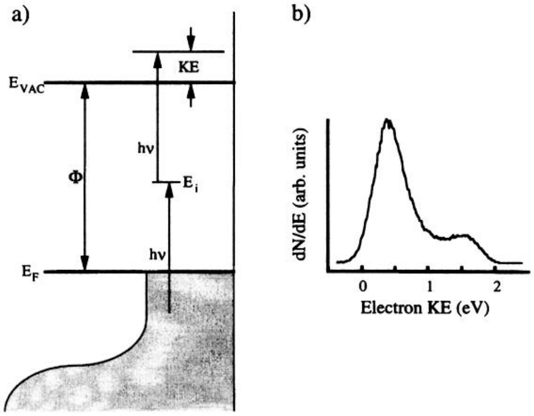

FIG. 1. Part (a) is a schematic representation of the two-photon process being measured. The shaded region indicates the density of occupied states. The photon energies used here access *s* electrons and the top of the *d* band. The work function Φ for Cu(100) is 4.6 eV, and the photon energy used in this study is 3.14 eV. Part (b) is the photoemission spectrum obtained with one beam blocked. The ~1.7-eV width of the spectrum (which is broadened to ~1.9 eV by the instrumental resolution of the energy analyzer) is obtained from the difference of the two-photon energy (6.3 eV) and the work function.