The role of occupied d states in the relaxation of hot electrons in Au

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We present first-principles calculations of electron-electron scattering rates of low-energy electrons in Au. Our full band-structure calculations indicate that a major contribution from occupied d states participating in the screening of electron-electron interactions yields lifetimes of electrons in Au with energies of $1.0 - 3.0\,\text{eV}$ above the Fermi level that are larger than those of electrons in a free-electron gas by a factor of ~ 4.5. This prediction is in agreement with a recent experimental study of ultrafast electron dynamics in Au(111) films (J. Cao *et al*, Phys. Rev. B **58**, 10948 (1998)), where electron transport has been shown to play a minor role in the measured lifetimes of hot electrons in this material.

Relaxation lifetimes of excited electrons in solids with energies below the vacuum level can be attributed to a variety of inelastic and elastic scattering mechanisms, such as electron-electron (e-e), electron-phonon (e-p), and electron-imperfection interactions.[1,2] Besides, when these so-called hot electrons are generated by absorption of an optical pulse, as occurs in the case of time-resolved two-photon photoemission (TR-2PPE) techniques,[3,4] electron transport provides an additional decay component to the photoexcited electron population. Since inelastic lifetimes of hot electrons become infinitely long as they approach the Fermi level, e-p scattering and the scattering by defects both play a key role in the relaxation process of electrons very near the Fermi level. However, in the case of hot electrons with energies larger than $\sim 0.5 - 1.0\,\text{eV}$ above the Fermi level, e-e interactions yield inelastic lifetimes that are in the femtosecond time scale and they provide the main scattering mechanism.

Experimental femtosecond time-resolved photoemission studies of electron dynamics have been performed in a variety of solid surfaces,[5-14] the role of e-e inelastic scattering and that of electron transport being difficult to identify. However, recent TR-TPPE experiments in Au(111) films with thicknesses ranging from 150 to 3000 Å have shown the relaxation from electron transport to be negligible and the hot-electron lifetime to be solely determined, at energies larger than $\sim 0.5 - 1.0\,\text{eV}$ above the Fermi level, by e-e inelastic scattering processes.[15] Hence, these measurements provide an excellent bench mark against which to investigate the importance of band-structure and many-body effects on electron dynamics in solids. Also, ballistic electron emission spectroscopy (BEES) has shown to be capable of determining hot-electron relaxation times in solid materials.[16]

In this paper, we report first-principles calculations of the energy-dependent inelastic lifetime of hot electrons in Au. We follow the many-body scheme first developed by Quinn and Ferrell[17] and by Ritchie,[18] but we now include the full band structure of the solid. This approach has already been successfully incorporated in the description of inelastic lifetimes of excited electrons in a variety of simple (Al, Mg, and Be) and noble (Cu) metals.[19,20] A similar methodology, which is also based on the GW approximation of many-body theory,[21] has been used by other authors to evaluate hot-electron lifetimes in Al and Cu.[22]

Our many-body scheme for the calculation of inelastic lifetimes in real solids has been described elsewhere.[19,20] For periodic crystals, the basic equation for the decay rate τ_i^{-1} of an electron in the state $\phi_{\mathbf{k},n_i}$ of energy $E_{\mathbf{k},n_i}$ is (we use atomic units throughout, i.e., $e^2 = \hbar = m_e = 1$)

$$\tau_i^{-1} = \frac{1}{\pi^2} \sum_{n_f} \int_{\text{BZ}} d\mathbf{q} \sum_{\mathbf{G},\mathbf{G}'} \frac{B_{if}(\mathbf{q}+\mathbf{G}) B_{if}^*(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2} \times \text{Im}\left[-\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega)\right], \qquad (1)$$

where $B_{if}(\mathbf{q}+\mathbf{G})$ represent the coupling between the hot-electron initial and final states [see Eq. (5) of Ref. 19], and $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega)$ are the Fourier coefficients of the inverse dielectric function of the solid, which we compute in the random-phase approximation (RPA).[23] $\mathbf{G}$ and $\mathbf{G}'$ represent reciprocal lattice vectors, the integration over $\mathbf{q}$ is extended over the first Brillouin zone (BZ), the sum over n_f is extended over the band structure for each wave vector in the first BZ, $\omega = E_{\mathbf{k},n_i} - E_{\mathbf{k}-\mathbf{q},n_f}$ is the energy transfer ($0 < \omega < E_{\mathbf{k},n_i} - E_F$), and E_F is the Fermi energy.

If one neglects crystalline local-field effects, Eq. (1) can be expressed as follows

$$\tau_i^{-1} = \frac{1}{\pi^2} \sum_{n_f} \int_{BZ} d\mathbf{q} \sum_{\mathbf{G}} \frac{|B_{if}(\mathbf{q}+\mathbf{G})|^2}{|\mathbf{q}+\mathbf{G}|^2} \frac{\text{Im}\left[\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)\right]}{|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)|^2}.$$

$$(2)$$

Here, initial and final states of the hot electron enter through the coefficients $B_{if}(\mathbf{q}+\mathbf{G})$. The imaginary part of $\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)$ represents a measure of the number of states available for the creation of an electron-hole pair involving a given momentum and energy transfer $\mathbf{q}+\mathbf{G}$ and ω, respectively, renormalized by the coupling between electron and hole states. The factor $|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)|^{-2}$ accounts for the dynamically screened e-e interaction.

The decay rate of Eqs. (1) and (2) depends on both the wave vector $\mathbf{k}$ and the band index n_i of the initial Bloch state. Since measurements of hot-electron lifetimes are reported as a function of energy and the proper choice of the wave vector $\mathbf{k}$ and the band index n_i is usually not easy to be determined, we define $\tau^{-1}(E)$ as the average of $\tau^{-1}(\mathbf{k},n)$ over all wave vectors and bands lying with the same energy in the irreducible wedge of the Brillouin zone (IBZ).

If all one-electron Bloch states entering both the coefficients $B_{if}(\mathbf{q}+\mathbf{G})$ and the dielectric function $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ were represented by plane waves and, at the same time, all energy bands were replaced by those of free electrons, then decay rates would not be direction-dependent and both Eqs. (1) and (2) would exactly coincide with the GW scattering rate of hot electrons in a FEG.[2] For hot electrons with energies very near the Fermi level ($E \sim E_F$) this result leads, in the high-density limit ($r_s \ll 1$),[24] to the well-known formula of Quinn and Ferrell[17] [see Eq. (7) of Ref. 19, which yields time in fs when E and E_F are expressed in eV]. The $r_s^{-5/2}$ scaling of hot-electron lifetimes predicted by this equation is found to be entirely originated in the density-dependent screening of e-e interactions [high electron densities yield a weaker interaction, $\sim r_s^{-3/2}$] and the density-dependent momentum of the hot electron [high electron densities yield a larger momentum and, therefore, a smaller number of available transitions, $\sim r_s^{-1}$].

Gold is a noble metal with entirely filled 5d-like bands. In Fig. 1 we show the energy bands of this face-centered cubic crystal. We see large differences between the band structure of this material and that of free electrons. Slightly below the Fermi level, at $E - E_F \sim 2\,\text{eV}$, we have d bands capable of holding 10 electrons per atom, the one remaining electron being in a free-electron-like band below and above the d bands. These d bands, which are concentrated within a width of $\sim 5.5\,\text{eV}$, are associated with the characteristic d-band wave functions at levels Γ'_{25} and Γ_{12}. Hence, a combined description of both delocalized $6s^1$ and localized $5d^{10}$ electrons is needed in order to address the actual electronic response of Au. The results presented below have been obtained by first expanding all one-electron Bloch states in a plane-wave basis and then solving the Kohn-Sham equation[25] of density-functional theory (DFT)[26] with all $6s^1$ and $5d^{10}$ Bloch states taken as valence electrons in the pseudopotential generation.[27] Thus, a kinetic-energy cutoff as large as 75 Ry has been required, thereby keeping ~ 1200 plane waves in the expansion of each Bloch state. Though all-electron schemes, such as the full-potential linearized augmented plane-wave (LAPW) method,[28] are expected to be better suited for the description of the response of localized d electrons, the plane-wave pseudopotential approach has already been successfully incorporated in the description of the dynamical response[29] and hot-electron lifetimes[19,20,22] of Cu.

The sampling over the BZ required for the evaluation of both the dielectric matrix and the hot-electron decay rate of Eqs. (1) and (2) has been performed on a $16 \times 16 \times 16$ Monkhorst-Pack (MP) mesh.[30] For hot-electron energies under study ($E - E_F \sim 1.0 - 3.0\,\text{eV}$), well-converged results have been found with the inclusion in the evaluation of the dielectric matrix of conduction bands up to a maximum energy of 25 eV above the Fermi level. The sums in Eqs. (1) and (2) have been extended over 15 $\mathbf{G}$ vectors, the magnitude of the maximum momentum transfer $\mathbf{q}+\mathbf{G}$ being well over the upper limit of $\sim 2\,q_F$ (q_F is the Fermi momentum).

Our full band-structure calculation of the average lifetime $\tau(E)$ of hot electrons in Au, as obtained from Eq. (1) with full inclusion of crystalline local-field effects, is presented in Fig. 2 by solid circles. The lifetime of hot electrons in a FEG with the electron density equal to that of $6s^1$ electrons in Au ($r_s = 3.01$) is exhibited in the same figure, as obtained from either Eq. (1) or Eq. (2) with the full RPA dielectric function of free electrons (solid line) and from the formula of Quinn and Ferrell (dotted line). Also plotted in this figure is the lifetime of hot electrons in Au(111) films, as determined from accurate TR-TPPE experiments (open squares).[15] The agreement between our full band-structure calculation and the experimental data is excellent, for all hot-electron energies under study.

Both band-structure (solid circles) and FEG (solid line) calculations presented in Fig. 2 have been carried out within the same many-body framework: The electron self-energy has been obtained in the GW approximation and *on-the-energy-shell* [deviations of the actual excitation energy from the independent-particle approximation have been neglected], and the RPA has been used to compute the dielectric function of the solid. Hence, the ratio (~ 4.5) between our calculated *ab initio* lifetimes and the corresponding FEG calculations unambiguously establishes the impact of the band structure of the crystal on the hot-electron lifetime.[31] Furthermore, since many-body effects beyond our GW-RPA scheme are expected to be within 20% of our calculations,[32] we conclude that large deviations of the experimental measurements from the FEG prediction are mainly due to band-structure effects. Nevertheless, one must be cautious with the comparison between our full band-structure calculations and the experiment. Since Au has a wide energy gap along the ΓL direction just over the Fermi level, the $k_\parallel = 0$ pho-

toemission in Au(111) cannot be associated, in the energy range under study ($E - E_F \sim 1.0 - 3.0\,\text{eV}$), with hot-electron Bloch states in the same direction, and therefore the proper choice of the wave vector $\mathbf{k}$ appears to be unclear. We have evaluated hot-electron lifetimes along various directions of the wave vector, and have found that differences between these results and the average lifetimes presented in Fig. 2 are within $\sim 20\%$, which gives support to our comparison with the experiment.[33]

In order to investigate the role that occupied d states plays in the relaxation of hot electrons in Au, now we neglect crystalline local-field effects and compute hot-electron lifetimes from Eq. (2). Scaled lifetimes $\tau(E) \times (E - E_F)^2$ of hot electrons in Au, as obtained from Eq. (2) by replacing the hot-electron Bloch states and bands entering $|B_{if}(\mathbf{q} + \mathbf{G})|^2$ by those of free electrons and the dielectric function in $|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)|^{-2}$ by that of a FEG with $r_s = 3.01$, are represented in the inset of Fig. 2 by open triangles. These calculated lifetimes, which have been obtained with full inclusion of the band structure of the crystal in the evaluation of $\text{Im}[\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)]$, are close to those obtained within the FEG model of the solid (solid line), showing that the combined effect of the density of states (DOS) available for e-h pair creation and the small overlap between d states below and sp states above the Fermi level nearly compensate. Hence, deviations of actual hot-electron lifetimes from FEG predictions are mainly originated in the deviation of the hot-electron momentum from the FEG prediction [the momentum of hot electrons depends on the actual DOS at the Fermi level] and the participation of d electrons in the screening of e-e interactions.

The effect of virtual interband transitions giving rise to additional screening is to largely increase the hot-electron lifetime in Au, as occurs in the case of Cu,[19] a noble metal with analogous electronic structure. Since the change $\delta\epsilon_1^b$ in $\epsilon_1(\omega)$ due to the presence of d electrons in the noble metals is found to be practically constant at low frequencies,[34,35] Quinn[36] treated the FEG as if it were embedded in a medium of dielectric constant $\epsilon_0 = 1 + \delta\epsilon_1^b$ instead of unity. The corrected lifetime is then found to be larger by roughly a factor of $\epsilon_0^{1/2}$, i.e., ~ 2.5 for both Cu and Au. Nevertheless, our first-principles evaluation of the wave-vector and frequency dependent dielectric matrix leads us to the conclusion that the role that occupied d states play in the screening of e-e interactions is much more important in Au than in Cu. This is an expected result, since Au $5d$ electrons lie further away from the nucleus than Cu $3d$ electrons, and $5d$ bands in Au are, therefore, more free-electron-like than $3d$ bands in Cu [d bands in Cu are concentrated within a width of $\sim 3\,\text{eV}$,[37] smaller than in the case of Au].

The result we obtain with full inclusion of the band structure of the crystal in the evaluation of Eq. (2), but still neglecting crystalline local-field effects, is represented in the inset of Fig. 2 by open circles. Our full band-structure calculation of Eq. (1) for Au is repre-

sented in the same figure by solid circles, showing that neglecting crystalline local-field corrections results in an overestimation of hot-electron lifetimes of $40\% - 50\%$. These crystalline local-field effects, which partially compensate the pronounced participation of d electrons in the screened e-e interaction, are due to large electron-density variations in this material.

In conclusion, we have presented full band-structure calculations of the inelastic lifetime of hot electrons in Au. We have found that a major contribution from occupied d states participating in the screening of e-e interactions yields lifetimes of electrons with energies of $1.0 - 3.0\,\text{eV}$ above the Fermi level that are larger than those of electrons in a FEG by a factor of ~ 4.5, in agreement with the experiment. The effect of virtual interband transitions giving rise to additional screening does not depend on whether the hot electron can excite d electrons [the d-band scattering channel opens at $\sim 2\,\text{eV}$ below the Fermi level] or not. On the other hand, the actual density of occupied states available for real transitions is found not to play an important role in the relaxation mechanism. Consequently, actual lifetimes approximately scale as $(E - E_F)^{-2}$, as in the case of a FEG. That lifetimes of hot electrons in Au can be fitted within this scaling behaviour has also been demonstrated by a theoretical analysis of electron-electron mean free paths in BEES experiments.[16]

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[32] Within a FEG model of the solid, short-range XC effects are found to yield lifetimes that are $\sim 5\%$ *shorter* than those obtained in the GW-RPA, while an expansion of the electron self-energy in the deviation of the actual excitation energy from its independent-particle counterpart yields lifetimes that are *longer* than those obtained on-the-energy-shell by $\sim 20\%$ (see Ref. 2).

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FIG. 1. Calculated band structure of Au along certain symmetry directions.

FIG. 2. Hot-electron lifetimes in Au. Solid circles represent our full *ab initio* calculation of $\tau(E)$, as obtained after averaging $\tau(\mathbf{k}, n)^{-1}$ of Eq. (1) over wave vectors and over the band structure for each $\mathbf{k}$. The solid line represents the lifetime of hot electrons in a FEG with $r_s = 3.01$, as obtained within the full GW-RPA. Open squares represent the experimental measurements of Ref. 15. The dotted line represents the prediction of Quinn and Ferrell. Differences between the FEG calculations represented by solid and dotted lines are due to the fact that the formula of Quinn and Ferrell is obtained for hot-electron energies very near the Fermi level ($E \sim E_F$) and in the high-density limit ($r_s \to 0$). The inset exhibits scaled lifetimes of hot electrons in Au. Open circles represent our calculation of $\tau(E)$, as obtained after averaging $\tau(\mathbf{k}, n)^{-1}$ of either Eq. (1) or Eq. (2) over wave vectors and over the band structure for each $\mathbf{k}$ and neglecting crystalline local-field corrections. Open triangles represent the result obtained from Eq. (2) by replacing hot-electron Bloch states in $B_{if}(\mathbf{q} + \mathbf{G})$ and $|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q}, \omega)|^{-2}$ by those of free electrons, but with full inclusion of the band structure of the crystal in the evaluation of $\mathrm{Im}[\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q}, \omega)]$.
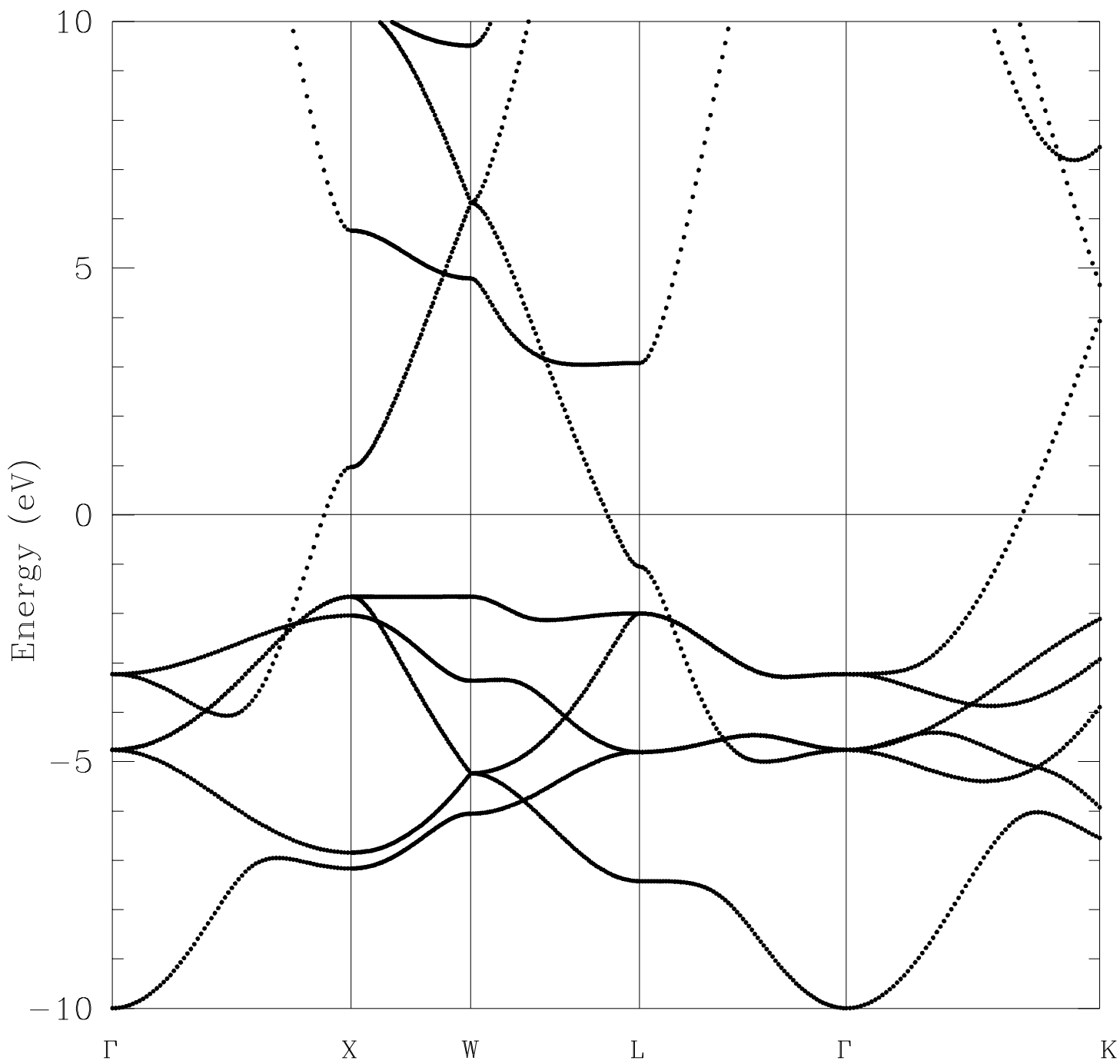
Au–(fcc)–BULK   (PW) LDA

Figure 2