Role of Spin-Flip Exchange Scattering for Hot-Electron Lifetimes in Cobalt

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The spin-dependent lifetimes of hot electrons in fcc Co films were studied by spin- and time-resolved two-photon photoemission. Even for excitation energies close to the Fermi level, we find almost identical lifetimes for majority and minority electrons. This result contradicts *ab initio* theories predicting 5 to 10 times longer lifetimes for the majority electrons in 3*d* ferromagnets. We provide direct experimental evidence that this discrepancy is caused by the dominance of exchange scattering in inelastic electron decay, in combination with the excitation of secondary electrons. The latter are inherent for all real materials and devices.

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Electrons excited to low energies above the Fermi energy E_F—the so-called hot electrons—play a key role, especially for magnetic materials. They carry spin-dependent electric currents in spin-valve systems which are relevant for spintronics applications [1]. Furthermore, they are essential for the giant-magnetoresistance (GMR) effect [2], exploited in read heads of advanced magnetic storage devices. In optical demagnetization experiments, hot electrons are created by absorbing the laser pump power and are then capable of triggering ultrafast demagnetization [3–5] as well as all-optical magnetic switching [6]. All the above processes depend on the lifetime of hot electrons and, in particular, its spin dependence. Neglecting higher-order effects, such as electron-hole scattering and spin-wave (magnon) emission, the lifetime of an excited electron is governed by the phase space available for its decay and for the concomitant excitation of a secondary electron [7,8]. The primary hot electron decays via inelastic electron-electron scattering whereby the energy is transferred to a secondary electron with identical or opposite spin [9]. The secondary electron reappears in the respective spin channel and thus represents an inherent contribution to the transient hot-electron population in all real materials—an effect which is not included in current theoretical models.

Spin- and time-resolved two-photon photoemission (SR-2PPE) measurements give direct access to the lifetime $\tau_\uparrow$ ($\tau_\downarrow$) of hot majority (minority) electrons. The technique is complementary to electron transport measurements [10], where the transmission through interfaces, momentum scattering, and unknown group velocities render lifetime analysis difficult. First SR-2PPE measurements of hot bulk electron lifetimes were performed by Aeschlimann *et al.* [11] on Co/Cu(001), in the energy range 0.6–1.1 eV above E_F. The derived lifetime ratios $\tau_\uparrow/\tau_\downarrow$ are smaller than predicted by *ab initio* theory. This calls for measurements closer to E_F, where even higher lifetime ratios (5–10) are predicted [12–16].

In this Letter we find an increase of the hot-electron lifetimes close to E_F, but with very small difference for majority and minority electrons. We experimentally prove that the origin of the similar behavior in both spin channels is the dominance of exchange scattering in inelastic electron decay in combination with the excitation of secondary electrons. In our experiments the minority part of the well-known Co(001) surface state $S_\downarrow$ [17,18] is used as a sensor: We follow the decay of laser-excited photoholes within $S_\downarrow$ that gives rise to characteristic secondary electrons with opposite spin.

As samples, we used 20 ML of Co, evaporated on Cu (001) at $T = 110$ K [19], subsequently annealed to 390 K to obtain single-crystalline fcc films with a well-ordered surface (work function 4.76 ± 0.02 eV). A Ti:sapphire laser oscillator is tuned to the fundamental wavelength $\lambda = 826$ nm and frequency tripled to $\lambda = 275$ nm. This enables us to measure hot electrons on the clean Co surface close to E_F. The lengths of the IR (UV) pulses is 35 (45) fs, $h\nu = 1.5$ eV ($3h\nu = 4.5$ eV), at a laser power of 200 mW (6 mW), focused into a 700 μm^2 (530 μm^2) spot. A cylindrical sector electron analyzer—energy resolution set to 50 meV, angular acceptance $\pm 5°$—in combination with a spin-polarization detector of SPLEED type [spin-polarized low-energy electron diffraction at W(100)] was used to obtain SR-2PPE spectra. In previous work we have established a Sherman function of $S = 0.23$–0.24. The value has been carefully evaluated studying the spin polarization and exchange splitting of image-potential states (IPS) [20]. For lower values than $S = 0.23$ we obtain unphysical spin polarizations $>100\%$. For larger values of S majority and minority spectra and thus the spin-dependent lifetimes become even more similar. In the present experiment the temporal stability of $S = 0.24$ is crucial and was routinely controlled measuring the exchange splitting of the $n = 1$ IPS. To eliminate asymmetries of the SPLEED detector each measurement is

repeated with the sample magnetized in the reversed direction.

Figure 1 shows energy- and spin-resolved spectra for overlapping pulses ($t_d = 0$ fs). The dominant feature is the IPS which shows an exchange splitting of $\Delta E_{ex} = 20$ meV, marked by the vertical lines at $E_{kin} \approx 0.85$ eV (upper energy scale). The IPS is populated by the UV and probed by the IR pulse (see excitation scheme in Fig. 1). Interchanging the pulse sequence, hot electrons close to E_F are accessed. In order to separate both excitation processes, we simulated the IPS signal solving optical Bloch equations [21]. This well-established density-matrix formalism calculates the optical polarization between the continuum of initial states, the intermediate state ($n = 1$ or hot electrons), and the final-state (photoelectron) as well as their transient populations.

Time-resolved measurements of majority (↑) and minority (↓) electrons are shown in Fig. 2 on a semilogarithmic scale. The electron energies are fixed to values of 0.28, 0.38, and 0.48 eV above E_F while varying t_d between −180 and 300 fs. In each spectrum, the constant background was determined at negative pump-probe delay and subtracted. For a consistent fit of the data set (including the statistical error of the data points), we varied the amplitudes of the following contributions: (i) To describe the hot electrons, we simulated TR traces with respective lifetimes $\tau_\uparrow$ and $\tau_\downarrow$ for the different $E - E_F$ values. (ii) The contribution of the off-resonantly excited IPS has the shape of a cross-correlation (CC) trace between IR and UV pulses. Its maximum is at zero delay and the width is given by the durations of the pump and probe pulses. These laser parameters are kept constant in all fits and have been independently determined as described above. The amplitude of the CC is hardly spin dependent. It is responsible for the edge of the time-resolved traces at negative delays whereas the lifetimes of the hot electrons determine the (linear) slope at positive delays, enabling us to separate both contributions. (iii) At large delays the majority spectra are dominated by an additional contribution. The origin is the decay of long-living photoholes in the minority surface state $S_\downarrow$ of Co(001) that leads to the observation of secondary electrons in the majority spin channel due to exchange scattering. This will be discussed in detail further below. The constant lifetime of $\tau = 170 \pm 5$ fs—independent of $E - E_F$—was determined in a simultaneous fit for all majority spectra. The contribution is strong for majority

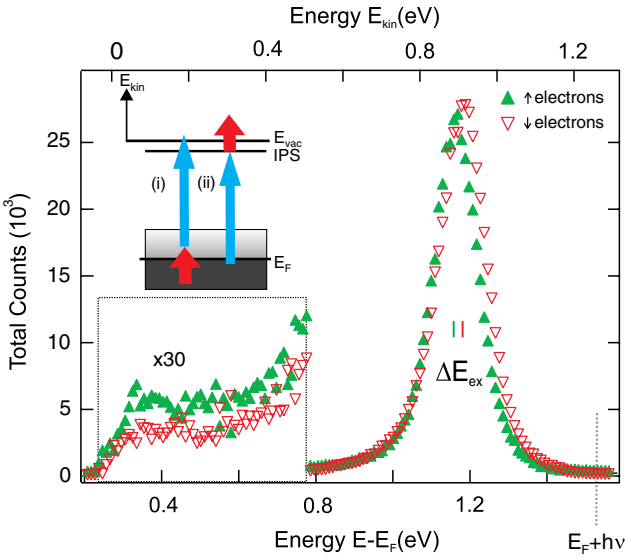

FIG. 1 (color online). Spin- and energy-resolved spectra, recorded at zero delay between laser pulses. Hot electrons and the $n = 1$ IPS are excited in parallel by reverted pump-probe processes as shown in the excitation scheme; for clarity the hot-electron signal is multiplied by 30 at small energies.

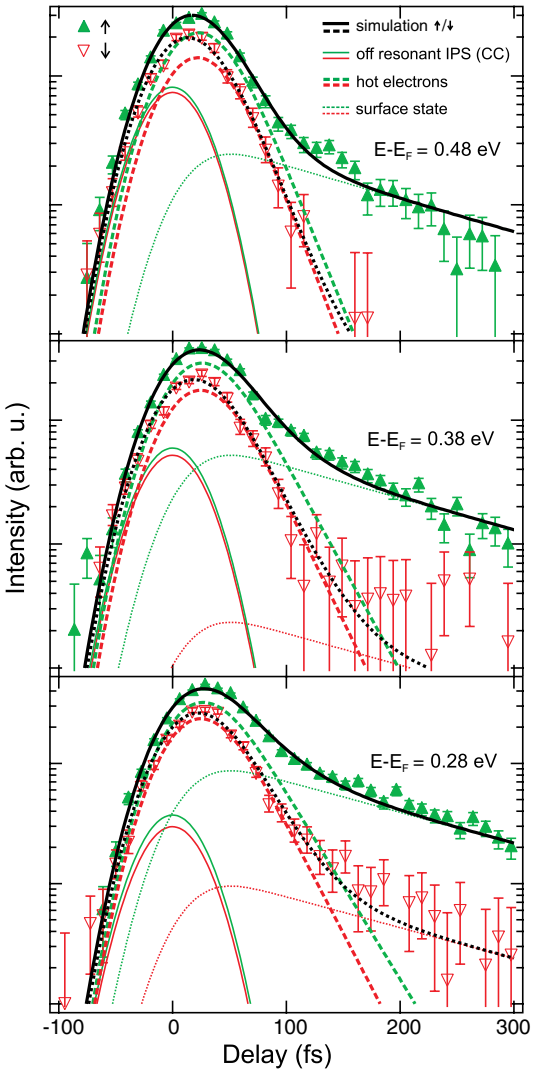

FIG. 2 (color online). Time-resolved measurements of hot majority (green filled triangles) and minority (red, empty triangles) electrons at different $E - E_F$. Optical Bloch equations were used to fit the experimental data (black solid lines) and to distinguish the different contributions: hot electrons (dashed lines), off-resonant IPS (light solid lines), and $S_\downarrow$ (light dashed lines).

electrons at low energies and negligible for minority electrons (except for a small contribution at 0.28 eV). With the above parameters each spectrum is fitted varying the three amplitudes and the lifetime of the hot electrons. Figure 3 summarizes the results of this least-square fit analysis. The lifetimes $\tau_\uparrow$ and $\tau_\downarrow$ of hot electrons (top panel) in the energy range of 0.28–0.68 eV above E_F are plotted, in good agreement with previous results for higher energies [11]. The error bars have been determined fitting the data with different hot-electron lifetimes. The lifetime of the hot electrons increases with decreasing energy, and majority electrons live longer than minority electrons. However, the lifetime ratio is significantly smaller than expected from phase-space arguments alone. At energies around 1 eV, the lifetime of majority electrons is about twice as long as that of minority electrons, as can be seen from the ratio $\tau_\uparrow/\tau_\downarrow$ (bottom panel). Towards E_F, $\tau_\uparrow$ and $\tau_\downarrow$ become very similar, contrary to the large difference in the majority and minority density of states (DOS), typical for the strong ferromagnets Co and Ni close to E_F. Therefore neither the free electron model of Ref. [8] [dashed lines in Fig. 3(a)] nor a fit of Eq. (22) in Ref. [8] to the full data set in Fig. 3(a) leads to reasonable agreement. This holds likewise for the model in Ref. [22]. Our observations point to the relevance of processes that equalize $\tau_\uparrow$ and $\tau_\downarrow$.

Close to E_F, all *ab initio* calculations predict much longer lifetimes for majority than for minority electrons. This is the case for bcc iron, if spin-wave emission is included in the $GW + T$ approach [23]. Likewise for fcc nickel, much larger spin-dependent lifetime ratios are predicted [15]. The experimental values for cobalt are between these calculated curves for majority and minority electrons. In Ref. [12] calculations of the imaginary part of the self-energy Σ were performed, with $1/\tau_{\uparrow\downarrow} = -(1/\hbar)\mathrm{Im}(\Sigma_{\uparrow\downarrow})$, for fcc and hcp Co for a much larger energy window. Close to E_F, their calculations show a significant difference between majority and minority electrons lifetimes, contrary to our findings. The comparison with theory shows that neither semiempirical nor state-of-the-art *ab initio* calculations properly include all relevant processes involved in the decay of an excited electron population in a real material such as Co.

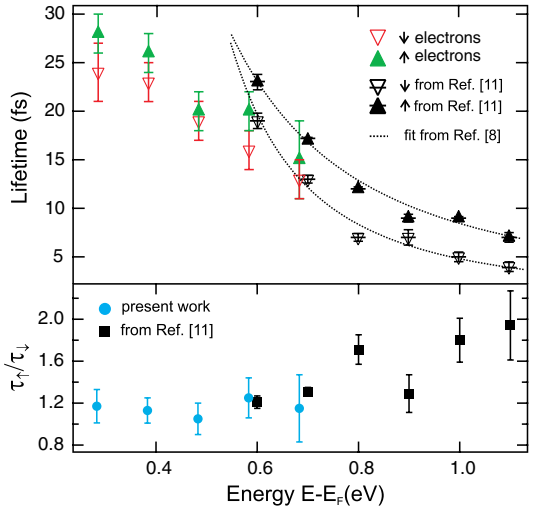

FIG. 3 (color online). Top panel: Lifetimes $\tau_\uparrow$ and $\tau_\downarrow$: present work (left), between 0.28 and 0.68 eV, and experimental results from Ref. [11] (including statistical error only) with fits from Ref. [8]. Bottom panel: lifetime ratio $\tau_\uparrow/\tau_\downarrow$.

Spin-flip exchange scattering is capable of equalizing the lifetimes of majority and minority hot electrons. As illustrated in Figs. 4(b) and 4(c) the exchange processes "mix" the phase space in the sense that majority electronic states are involved in the decay of an minority electron and vice versa. The exchange-scattered electrons inherently reappear as secondary electrons in the opposite spin channel. Such virtual spin-flip processes have up to now only been observed when spin-polarized electrons are scattered at ferromagnetic surfaces [9,24]. Third and higher-order effects [wiggly line in Figs. 4(b) and 4(c)] describe the contribution of multiple, virtual electron-hole pair excitations in opposite spin channels, i.e., spin-wave (or magnon) emission (see, e.g., review [16]). In Refs. [13,25], the relevance of spin-flip exchange scattering (neglecting secondary electrons) is theoretically analyzed for pseudo Fe, Co, and Ni, i.e., within a simplified one-*d*-band model. The authors find the maximal contribution to $\mathrm{Im}(\Sigma)$ around electron energies of $E - E_F = 3$ eV. They furthermore conclude that for small excess energies relevant for the present work, spin-wave emission dominates electron decay.

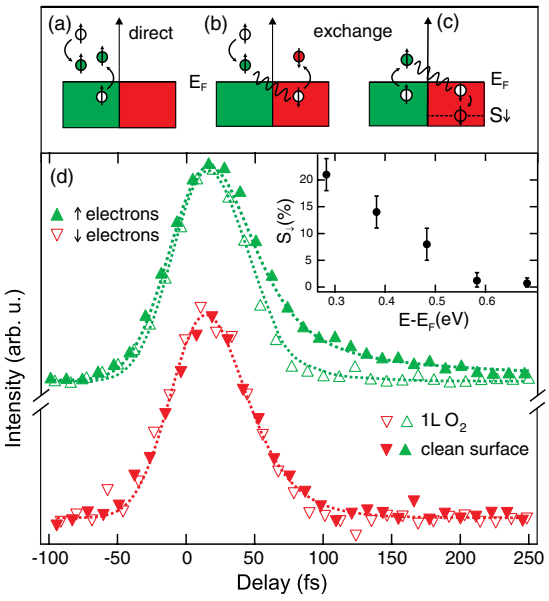

FIG. 4 (color online). Scheme of (a) direct and (b),(c) exchange scattering. (d) Time-resolved measurements at $E - E_F = 0.34$ eV: For the clean Co(001) surface (filled symbols) the long-living component in the majority channel is visible which originates from $S_\downarrow$. A quenching of $S_\downarrow$ by dosing 1 L of oxygen (open symbols) leads to similar behavior for majority and minority electrons. Inset: relative contribution (peak area) of $S_\downarrow$ to the majority electron counts.

Our SR-2PPE results provide direct experimental evidence of a spin-flip exchange-scattering channel involving the minority Co surface state $S_\downarrow$: With the IR laser pulse, we excite not only electron-hole pairs in the bulk but also photoholes in $S_\downarrow$. The latter is located at the binding energy of 0.45 eV below E_F [17,18]. The photoholes in the surface state recombine with minority electrons with higher energies originating from bulk states in the energy window between $S_\downarrow$ and E_F, as schematically shown in Fig. 4(c). The small overlap between $S_\downarrow$ and bulk states accounts for the long lifetime of these photoholes which due to spin conservation in Coulomb scattering must be filled by minority bulk electrons. However, to conserve energy and momentum, the decay of the photohole in $S_\downarrow$ must be accompanied by the generation of a secondary electron-hole pair. We note that this secondary excitation involves bulk electrons and can occur either in the same or the opposite spin channel. Furthermore, a secondary process of the same type occurs upon the decay of hot electrons. Multiple scattering between the finally excited bulk electron and hole in opposite spin channels [wiggly line in Fig. 4(b) and 4(c)] describes the contribution of bulk spin waves to the decay of excited electrons [14].

We experimentally prove that the long-living contribution to the lifetimes of the majority hot electrons arises from exchange scattering via $S_\downarrow$ by modifying the Co(001) surface electronic structure: The adsorption of oxygen suppresses the $S_\downarrow$ feature [17,18]. Figure 4(d) shows hot-electron measurements for $E - E_F = 0.34$ eV for the clean surface with a significant long-living contribution for the majority electrons (filled symbols) and after dosing 1 L (1 L $\approx$ 133 Pa $\times$ 10^{-6} s) oxygen (open symbols). The direct comparison of the majority signal (top) shows that the long-living contribution vanishes upon oxygen adsorption while minority electrons show a similar behavior with or without oxygen (bottom). The same effect is obtained in hot-electron spectra on an as-grown Co film with a rough surface and a weakly developed surface state.

The inset of Fig. 4 shows the amount of the $S_\downarrow$-induced contribution to the majority spectra. It is strong up to 0.45 eV above E_F, corresponding to the maximal energy gain of a minority electron recombining with a hole in $S_\downarrow$. Above 0.45 eV this contribution is negligible. The constant lifetime of 170 fs of the secondary electrons in the minority channel, independent of $E - E_F$, reflects the lifetime of the photoholes in $S_\downarrow$. The experimental data presented in Fig. 2, clearly prove that for low-energy transfer $\Delta E \leq 0.5$ eV exchange scattering dominates. Processes capable of equalizing the lifetimes of majority and minority hot electrons, similar to the observed exchange scattering via $S_\downarrow$, will occur with a significantly high probability if solely bulk states are involved.

In summary, our SR-2PPE experiments directly prove that spin-flip exchange scattering in combination with the excitation of secondary electrons is crucial for the lifetimes of hot electrons. The observation of almost identical, i.e., spin-independent lifetimes for energies close to E_F leads to the conclusion that spin-flip exchange scattering is dominant for small energies. Our experimental results prove that secondary electrons contribute significantly if not dominantly to the excited electron population and as such play a crucial role in all real materials and applications. The energy range we investigated is of particular importance for the fundamental understanding of the microscopic processes that govern ultrafast magnetization dynamics as well as for spin-dependent transport relevant for spintronics and GMR.

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