Competing spin transfer and dissipation at Co/Cu(001) interfaces on femtosecond timescales

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By combining interface-sensitive non-linear magneto-optical experiments with femtosecond time resolution and ab-initio time-dependent density functional theory, we show that optically excited spin dynamics at Co/Cu(001) interfaces proceeds via spin-dependent charge transfer and back-transfer between Co and Cu. This ultrafast spin transfer competes with dissipation of spin angular momentum mediated by spin-orbit coupling already on sub 100 fs timescales. We thereby identify the fundamental microscopic processes during laser-induced spin transfer at a model interface for technologically relevant ferromagnetic heterostructures.

The interaction of femtosecond (fs) laser pulses with magnetically ordered materials leads to magnetization dynamics on femto- to picosecond (ps) timescales in a highly non-equilibrium regime. Effects like ultrafast demagnetization [1, 2], all-optical switching [3, 4], and coherent control of magnons [5, 6] are highly relevant for potential future ultrafast spintronics applications. In particular, laser-driven spin-dependent charge currents on nm length scales induce fs spin transport in ferromagnetic (FM)/paramagnetic (PM) metallic heterostructures [7–10], which are the building blocks for spintronic devices, and chemically inhomogeneous ferrimagnetic alloys [11] exhibiting all-optical switching.

However, the role of microscopic processes at the interfaces of heterostructures is far from understood. Photoinduced charge transfer which includes excitation and relaxation of charge carriers, potentially involving nuclear motion, is fundamental in such heterosystems and highly dynamic [18–20]. Spin injection, i.e. spin-dependent charge transfer, further becomes important at FM/PM interfaces as well as symmetry breaking leading to a modification of spin-orbit coupling (SOC). Control over these spin currents opens up a widely inaccessible field of magnetization control by light pulses, e.g. ultrafast tuning of the magnetic order [22]. However, due to the complexity of addressing spin-dependent charge transfer processes at FM/PM interfaces directly on their intrinsic time and length scales, and identifying competing local loss mechanisms of spin polarization [24–29] and their microscopic origin, a full control of ultrafast non-local spin dynamics remains elusive.

In this Letter, we overcome this limitation by combining interface-sensitive femtosecond time-resolved non-linear magneto-optics [30–34] with ab-initio time-dependent density functional theory calculations on the identical epitaxial interface system, namely Co/Cu(001). TDDFT provides a parameter-free description of non-equilibrium dynamics, and the underlying mechanisms are not assumed but rather emerge from the theory. In particular, we go beyond a model description based on bulk transport properties such as superdiffusive transport [8]. We directly compare our ab-initio description with experiment and are able to distinguish all relevant microscopic processes during spin injection at the Co/Cu(001) interface. We showcase the competition of photo-excited
spin transfer from Co to Cu and back transfer from Cu to Co as well as demagnetization by SOC-mediated spin flips, all within the time interval shorter than 100 fs. Our results present a crucial step towards solving the critical open question of the role of the interface in ultrafast spin transport and competing elementary processes in FM heterostructures.

We become exclusively sensitive to the Co/Cu(001) interface by studying ultrathin films of 3 and 5 monolayer (ML) thickness and employing second harmonic generation (SHG) [30, 35] as a probe, which in centrosymmetric media is generated at interfaces only, where the inversion symmetry is broken. Co/Cu(001) films with epitaxial, atomically sharp interfaces [30, 37] are prepared, characterized, and measured in situ at room temperature in ultrahigh vacuum at a pressure smaller than 10^{-10} mbar. In a pump-probe experiment using 35 fs (FWHM) laser pulses with 800 nm wavelength, we analyze laser-induced magnetization dynamics with SHG at 400 nm wavelength after excitation at an incident pump fluence F = 4 ± 2 mJ/cm². Our films are magnetized parallel to the sample surface, perpendicular to the optical plane, and we detect SHG of the probe pulse in transversal geometry, see figure 1. From the second harmonic (SH) intensities I² even/odd for opposite orientations of the magnetization M we derive the SH fields, |E²_{even/odd}| ∝ \sqrt{I²_{even/odd}}, which behave even and odd with reversal of M, respectively, and are considered magnetization-independent and -dependent for E²_{even} >> E²_{odd} [30, 38, 39]. The time-dependent changes of E²_{even,odd} are normalized to their respective values before laser excitation and are represented by ΔE²_{even,odd} = (E²_{even,odd}(t)/E²_{even,odd}(t<0)) - 1, which measure charge and spin dynamics separately. For further details see [35].

We theoretically analyze the spin-dependent microscopic processes contributing to laser-induced spin dynamics with parameter-free, fully ab-initio time-dependent density functional theory (TDDFT). Our TDDFT calculations were performed for slabs of 3 or 5 ML Co on top of 7 ML Cu(001), and a pump laser pulse of 35 fs (FWHM) pulse length, 800 nm wavelength (1.55 eV photon energy) and F = 0.25 mJ/cm². This pump fluence is equal to the fraction of the experimentally employed fluence which is absorbed in the Co/Cu(001) heterostructure. In this way, we properly account for the fact that ≈ 94 % of the incident pump fluence is reflected from the sample surface. This could not otherwise be taken into account, as calculating the coupled dynamics of the electronic system and Maxwell’s equations is too computationally demanding. As implemented in the ELK code [40-42] using the full potential linearized augmented-plane-wave method, we treat the time-dependent Kohn-Sham orbitals as two-component Pauli spinors as follows:

\[ i \frac{\partial \psi_j(r,t)}{\partial t} = \left[ \frac{1}{2} \left( -i \nabla + \frac{1}{c} A_{ext}(t) \right)^2 + v_s(r,t) \right] \psi_j(r,t) \]

(1)

with σ referring to the Pauli matrices. The Kohn-Sham effective potential \( v_s(r,t) = v_{\text{ext}}(r,t) + v_{\text{ex}}(r,t) \) consists of the external potential \( v_{\text{ext}} \), the classical electrostatic Hartree potential \( v_{\text{H}} \), and the exchange-correlation (XC) potential \( v_{\text{xc}} \). While the Kohn-Sham magnetic field is \( B_s(r,t) = B_{\text{ext}}(r,t) + B_{\text{xc}}(r,t) \), \( B_{\text{ext}}(r,t) \) being the magnetic field of the laser pulse and \( B_{\text{xc}}(r,t) \) the XC magnetic field. We use the adiabatic local spin density approximation for \( B_{\text{xc}}(r,t) \), see [41]. The last term

FIG. 2. Pump-induced relative changes in second harmonic fields ΔE²_{even} (a) and ΔE²_{odd} (b) for 3 (circles) and 5 ML Co/Cu(001) (squares). Black lines indicate the pump-probe cross-correlation (CC) measured at the sample surface. It is shown inverted in (a). In addition, solid lines show (a) the relative change of spin-integrated charge carriers \( n_{\text{Co}} \) and (b) the relative change of the Co magnetic moment as calculated by TDDFT. Data for different Co thicknesses are vertically offset for display. The inset depicts ΔE²_{odd} for longer delays.
Magnetic moment induced in Cu μCu by spin transfer across the interface.

in Eq. 1 represents spin-orbit coupling. \( A_{\text{ext}}(t) \) is the vector potential representing the pump field. Since we only time-propagate the electronic system while keeping the nuclei fixed (Born-Oppenheimer approximation), our comparison with experiment focuses on the first \( t \approx 100 \) fs after optical excitation. At later times coherent \(^{45}\) and incoherent \(^{20,44}\) lattice excitations become important.

Experimental results are shown in Fig. 2 for 3 and 5 ML Co/Cu(001), together with the pump-probe cross correlation (CC) measured on the sample surface, which indicates the experimental time resolution. \( \Delta \mu \) quantifies the flow of optical excitation \( \Delta \mu_{\text{Co}} \), with and without SOC are given. Right: Magnetic moment induced in Cu μCu by spin transfer across the interface.

FIG. 3. Left: Comparison of the time-dependent change of magnetic moment for 3 ML Co/Cu(001) as observed in experiment by \( \Delta \mu_{\text{Co}} \) and by TDDFT calculations. The relative changes (normalized to values \( \mu(t < 0) \) before excitation) of the total spin moment in Co/Cu(001) \( \Delta \mu \) as well as of the Co contributions \( \Delta \mu_{\text{Co}} \) with and without SOC are given. Right: Magnetic moment induced in Cu μCu by spin transfer across the interface.

We moreover observe a larger pump-induced decrease in \( \mu_{\text{Co}}(t) \) than in \( \mu(t) \) at any given \( t \). The difference of \( \mu(t) \) and \( \mu_{\text{Co}}(t) \) provides the dynamics of the spin moment induced in Cu μCu(t), shown in Fig. 3 (right). \( \mu_{\text{Co}}(t) \) reaches its maximum at \( t = 35 \) fs and recedes on longer times. In the same way as the Co demagnetization at \( 35 \) fs \( t < 100 \) fs, this reduction is due to the coupling of both spin channels by SOC. Electron-electron scattering then leads to spin-flip processes and spin moment loss. Based on our TDDFT calculations we estimate the spin injection efficiency from Co to Cu...
before SOC-mediated spin flips start to dominate by \( \frac{\mu_{\text{Cu}(35 \text{ fs})} - \mu_{\text{Cu}(t<0)}}{\mu_{\text{Cu}(35 \text{ fs})} - \mu_{\text{Cu}(t<0)}} \). We obtain a spin injection efficiency of 40\% (25\%) for 3 (5) ML Co/Cu(001).

The dynamics of the spin-integrated charge carriers in Cu shown in Fig. 4(a) reinforces that the dynamics in the initial \( \approx 35 \text{ fs} \) are driven by charge transfer, as the pump-induced change saturates after this time. Fig. 4(b) displays the calculated time-dependent change of the number of majority (↑) and minority (↓) carriers in the Co (\( n_{\text{Cu}} \)) and Cu (\( n_{\text{Cu}} \)) layers. The increase of \( n_{\text{Cu}} \) simultaneous with a decrease of \( n_{\text{Cu}} \) is the consequence of spin transfer from ferromagnetic Co to paramagnetic Cu. However, the increase in Cu is much weaker than the decrease in Co, indicating the role of competing SOC mediated spin-flips, which limit the majority spin injection efficiency from Co to Cu. The two different rates of change of \( n_{\text{Co}} \) and \( n_{\text{Cu}} \) before and after \( \approx 35 \text{ fs} \) indicate that the dominant microscopic process changes from spin transfer across the interface to local spin flips mediated by SOC at this point of time. The turning point at \( \approx 35 \text{ fs} \) coincides with the pump pulse length, which suggests that spin transfer dominates as long as the pump pulse excites further carriers.

Moreover, we note that \( n_{\text{Cu}} \) increases more weakly than its counterpart \( n_{\text{Cu}} \) decreases. This behavior is explained by a back-transfer of minority carriers from Cu to Co, which supports the ultrafast demagnetization in the Co film. We explain this back-transfer by a resonant optical excitation with the employed 1.5 eV pump photon energy from occupied Cu minority 3d states to unoccupied Co minority 3d states. As depicted in Fig. 4(c), the electronic density of states (DOS) supports such an optically driven minority spin back-transfer from Cu to Co only directly at the interface, where hybridization of Cu and Co generates new Cu 3d states closer to the Fermi energy \( E_F \) than in bulk Cu \([49, 50]\). This finding indicates that optically excited spin transfer is determined by the available electronic states around \( E_F \), which can be tuned by choice of substrate and/or pump laser frequency.

Inclusion of spin-dependent charge transfer from the substrate and the actual interface electronic structure distinguishes our ab-initio approach from model calculations such as the superdiffusive spin transport model \([8, 51]\), which in contrast mainly accounts for spatial transport gradients in films based on spin-dependent lifetimes and velocities in FM only. This Cu to Co back-transfer demonstrates that spin-dependent charge transfer at interfaces can contribute significantly to ultrafast spin dynamics. Therefore, it is not sufficient to consider spin-dependent, hot electron lifetimes as input for modeling laser-induced spin transport, but spin-dependent charge transfer excitation across interfaces contributes in addition. Caution is warranted when spin-dependent lifetimes are analyzed in ultrathin FM films due to possible contributions of non-local spin transfer at interfaces.

We find that SOC-mediated spin flips can occur on sub 100 fs timescales as reported in literature for model calculations without accounting for the excitations of phonons \([24, 25]\). This timescale is much faster than assumed in models based on Elliott-Yafet-like phonon-mediated spin-flip scattering \([44]\), and might therefore be closer to the rate-limiting process in ultrafast demagnetization. On the other hand, SOC mediates the interaction of the magnetic moment with the lattice, which will inevitably act as a sink for the angular momentum \([29]\).

Our present work indicates that three different microscopic processes dominate ultrafast demagnetization at Co/Cu(001) interfaces during subsequent time intervals, starting with spin transfer and back-transfer at \( t < 35 \text{ fs} \), followed by SOC mediated spin-flips during 35 fs < \( t < 100 \text{ fs} \), and finally phonon-mediated processes. Phonon excitation can induce further demagnetization \([44, 52]\) but also relaxation as experimentally observed here, when heat transport from the FM layer into the PM substrate leads to dissipation of excess energy.

In summary, we have disentangled the competing microscopic processes occurring after fs optical excitation of Co/Cu(001) interfaces. From a comparison of ab-initio TDDFT and interface-sensitive fs time-resolved SHG, we identify spin transfer between Co and Cu governing the dynamics in the first 35 fs. Subsequently SOC mediated spin flips reduce the overall spin polarization by dissipation to the lattice within 100 fs, and thus limit the efficiency of spin-polarized charge transfer. Our finding of a minority spin back-transfer from Cu to Co due to a resonant optical transition in the interface layers’ DOS opens new possibilities for optical control of spin dynamics on fs timescales via tunable laser pulses.

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