Femtosecond Electron and Spin Dynamics in Ni/W(110) Films

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The collapse of the magnetic exchange splitting in 7 monolayer thick epitaxial Ni/W(110) films following a femtosecond laser pulse was measured using time-resolved photoemission spectroscopy. Ultrafast demagnetization during the laser induced hot electron cascade proceeds via spin-flip excitations with a relaxation time constant of 300 ± 70 fs. At longer times the electronic system cools down and the magnetization is finally reestablished with a time constant of 3.2 ± 0.2 ps.

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Understanding the energy transfer between charge, orbital, and spin degrees of freedom is a central topic for many fields of solid state physics. Recent advances in fs laser based spectroscopy offer the exciting prospect of real-time studies far from thermal equilibrium. In this case the various interactions may be separated by the different energy relaxation rates that depend on the interaction strengths.

For the case of magnetic switching in ferromagnets the response of the sample spins to an external magnetic field takes place on the ps time scale [1]. It is ultimately governed by the spin-lattice relaxation time, i.e., the transfer of angular momentum to the solid [2]. Much faster spin dynamics is induced by the stronger exchange interaction. For excited hot electrons in ferromagnetic materials spin dependent lifetimes of several fs [3] and fs spin precession around an effective exchange field were reported [4]. In this case the total magnetic moment of all spins in the material remains unchanged. On an intermediate time scale the relatively weak spin-orbit coupling is thought to be responsible for a conversion of spin into orbital angular momentum. This should lead to an ultrafast reduction of the sample magnetization following the fs relaxation of excited unpolarized electrons.

Although of direct relevance for establishing the ultimate writing speed in magneto-optical data storage devices the time scale for such a process remains elusive [5–8]. Experimentally this uncertainty may arise from the fact that it is difficult to separate fs electron and spin dynamics with the widely employed magneto-optical techniques [9]. As a consequence it is still a matter of debate whether this demagnetization is of purely electronic origin, i.e., caused by spin-flip scattering [5,7] and an increased electronic temperature [8], or whether angular momentum is transferred to quasiparticles such as phonons and magnons [6]. Furthermore, it has been suggested theoretically that spin-orbit coupling alone may be too weak and that it is rather an interplay between spin-orbit forces and a strong laser field that leads to an ultrafast sample demagnetization [10].

In this Letter we use time-resolved photoemission spectroscopy with 6 eV photons to independently probe the ultrafast electron and magnetization dynamics in ultrathin single crystalline Ni/W(110) films. Following the absorption of 1.5 eV photons from fs laser pulses we find a relaxation of the hot electrons above the Fermi level, E_F, via electron-hole pair generation. The excited electron system thermalizes within 0.5 ps. During that time we observe a collapse of the magnetic exchange splitting for the Ni $3d$ valence states with a time constant of 300 ± 70 fs. This represents the first direct measurement of an ultrafast demagnetization process in ferromagnets. Our data indicate that after about 2 ps electrons and lattice are in thermal equilibrium. The magnetic exchange splitting is reestablished with a time constant of 3.3 ± 0.2 ps. This process seems to be only marginally dependent on the electronic temperature evolution which points to a mayor influence of electron-magnon scattering.

The experimental setup is shown schematically in the inset of Fig. 1 and is described in detail in Ref. [11]. Photoelectrons were detected with a time of flight technique of 30 meV energy resolution along the $\overline{\Gamma}\,\overline{K}$ azimuth at emission angles of 30° and 40° leading to identical results. They were generated by laser pulses of 6 eV photon energy and 180 fs duration. Each probe pulse was preceded by a laser pulse of 1.5 eV photon energy and 85 fs duration. These pump pulses with a fluence of 13 mJ/cm^2 were used to excite electrons above E_F but were not intense enough to generate photoelectrons. We found that a photoemission background due to multiphoton absorption events could be strongly suppressed by a well-ordered and defect-free surface. The surface roughness could be very sensitively monitored from the position and width of Ni image potential states. The W(110) substrate was cleaned by flashes up to 2300 K. Ni was evaporated at a rate of 1 monolayer (ML)/min while the sample cooled down to room temperature. At a Ni coverage of 7 ML the electronic structure was similar to that of Ni(111) [12,13] as judged from 6 eV photoemission spectra.

Figure 1 shows typical 6 eV photoemission spectra taken at an emission angle of 40° for various pump-probe time delays. Although the high negative binding energy cutoff occurs close to E_F due to the relatively small

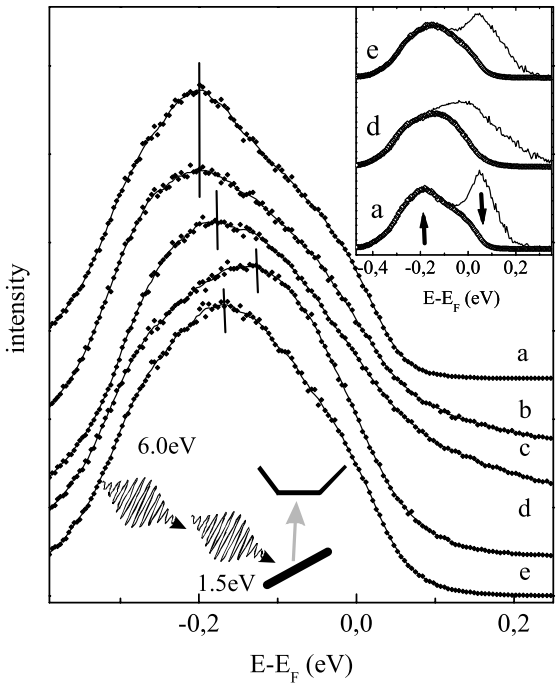

FIG. 1. Photoelectron spectra (dots and lines) taken with 6 eV probe laser pulses each preceded by a 1.5 eV pump laser pulse for pump-probe time delays of (*a*) −1 ps, (*b*) 0 ps, (*c*) 0.1 ps, (*d*) 1 ps, and (*e*) 4 ps. The binding energy of the majority spin state relative to the Fermi level, E_F, is marked by vertical lines. The lower inset depicts the experimental setup. The upper inset shows spectra (*a*), (*d*), and (*e*) (symbols). Lines represent the spectra divided by the Fermi function for the obtained electronic temperatures of 343, 595, and 423 K, respectively. The assignment of the observed peaks to majority (spin up) and minority (spin down) states is indicated by arrows.

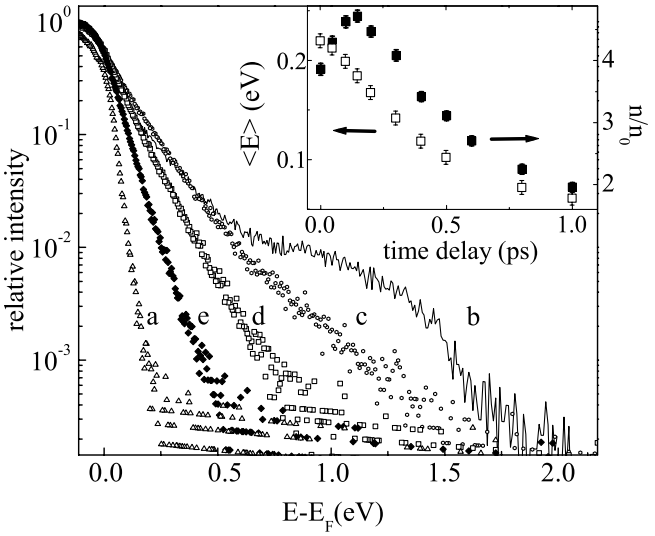

FIG. 2. Log plots of the photoemission intensity above the Fermi level, E_F, for pump-probe time delays of (*a*) −1 ps, (*b*) 0 ps, (*c*) 0.2 ps, (*d*) 0.4 ps, and (*e*) 0.8 ps. A linear behavior in this plot indicates that the electron distribution can be described by a Fermi function. The slope of this line corresponds to the temperature. The inset shows the number of excited electrons, n/n_0, obtained from the total photoemission intensity above E_F (solid symbols) normalized to spectrum (*a*) and the mean electron energy, $\langle E \rangle$, above E_F (open symbols) vs time delay.

photon energy, a dispersing peak (marked by vertical lines) is clearly discernible. The spectrum for −1 ps time delay is reproduced in the lower half of the Fig. 1 inset (solid line). It is identical to spectra taken only with 6 eV laser pulses. Following Ref. [14] we divided it through the Fermi function which was obtained by fitting to the data at binding energies above 0.2 eV. The resulting symmetrized spectrum (lines) displays two peaks separated by 230 ± 50 meV. This value is very close to the magnetic exchange splitting obtained for Ni previously [14–16]. We found that the peak separation decreased to zero by heating the sample above the Curie temperature of 480 K [17] (not shown) in agreement with the known temperature dependent quenching of the Ni magnetic moment [14,15]. We, therefore, assign the peak marked in Fig. 1 to the occupied majority spin state of the exchange split 3*d* bands which are responsible for ferromagnetism in Ni [14].

The hot electron dynamics can be seen in Fig. 2 where the photoemission intensity from above E_F is plotted for various pump-probe time delays. At negative time delays the spectrum (*a*) shows merely the thermal electronic population of nominally unoccupied states. This changes dramatically near time zero [spectrum (*b*)] when the laser pump pulses populate states up to 1.5 eV above E_F. Because of the finite width of the laser pulses electronic relaxation already sets in during the pulse duration leading to an increasing population of states further towards E_F. This process can be followed in detail with increasing pump-probe time delay [spectra (*c*)–(*e*)]. The center of the hot electron distribution shifts towards E_F. After about 0.5 ps the distribution resembles very closely a Fermi function in thermal equilibrium. The inset of Fig. 2 shows the time evolution of the integrated photoemission intensity (solid symbols) above E_F which is a measure of the number of excited electrons per atom, n. The data are normalized to the number of thermally activated hot electrons per atom, n_0, i.e., before laser excitation occurs [spectrum (*a*)]. n/n_0 initially increases. This is mainly caused by the filling of unoccupied minority spin states as can be seen by the crossing of curves (*b*) and (*c*) in Fig. 2 at an energy of 0.2 eV above E_F. After 0.15 ps n/n_0 decreases monotonously. The initial increase of n/n_0 is correlated to the fast decay of very hot electrons 0.8–1.5 eV above E_F [see curves (*b*) and (*c*)]. The inset of Fig. 2 also shows the temporal evolution of the mean energy, $\langle E \rangle$, of electrons above E_F (open symbols).

Results are summarized in Fig. 3. The solid line represents the transient population of states 1.5 eV above E_F. It corresponds to the temporal overlap between pump and

probe laser pulses since the electronic lifetimes for these states are only a few fs [3]. The binding energy of the occupied majority spin states (open and solid diamonds) shows distinct variations with pump-probe time delay. Fits of exponentials (dotted lines) result in time constants of 300 ± 70 fs and 3.3 ± 0.2 ps for the peak shift towards E_F and away from it, respectively. At time delays longer than about 0.5 ps the hot electron distribution (see Fig. 2) can be quite well described by a Fermi function. This indicates that the electronic system is thermalized and we can determine an effective electronic temperature. The obtained values are shown in Fig. 3 (open squares). After an initial rapid decrease the electronic temperature levels off around 2 ps time delay and remains almost constant at 410 ± 30 K up to the largest measured time delays of 9 ps.

We discuss these results in terms of energy transfer between quasiparticles such as electronic excitations, Stoner excitations, magnons, and phonons [5,6]. Consider first the electronic system. Initially energy is pumped into electron-hole excitations by the absorption of 1.5 eV photons. This leads to the transient population of electronic states above E_F as observed in Fig. 2. The generation of holes is evident from the transfer of spectral weight away from the majority spin photoemission peak below E_F in Fig. 1 [see spectra (*a*) and (*b*)]. We can calculate the number of excited electrons using an estimate for n_0. The symmetrized spectrum (*a*) (lines) in the lower half inset of Fig. 1 reflects the majority (minority) 3*d* density

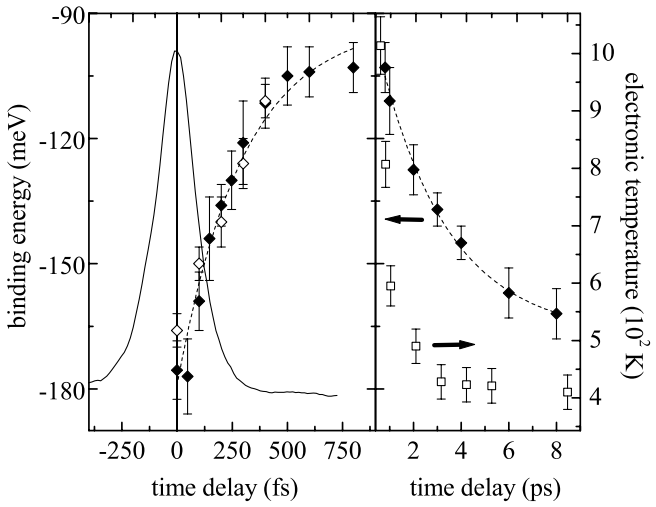

FIG. 3. Binding energy of the majority spin state (diamonds) and electronic temperature (open squares) vs pump-probe time delay. Solid and open diamonds are photoemission data obtained for emission angles of 40° and 30°, respectively. The binding energy was determined from a parabolic fit near the peak maxima to the raw data such as the ones shown in Fig. 1. The solid line represents the transient electron population of states 1.5 eV above E_F (see Fig. 2). Dotted lines are exponential fits to the data.

of states which are known to contain about one electron (hole) per atom in the hole pockets near the *L* point of the Ni Brillouin zone probed in our experiment. This results in a value of $n_0 = 0.11$ electrons/atom. During the first 0.15 ps the number of excited electrons increases from $n = 0.4$ to 0.5 electron/atom as seen in the inset of Fig. 2. The average energy of an excited electron is reduced from $\langle E \rangle = 220$ meV to 180 meV during the same time interval. This implies that the total hot electron energy per atom remains nearly constant up to 0.15 ps at a value of about $n\langle E \rangle = 95$ meV/atom. It seems reasonable to assume that this amount of energy was initially pumped into the electronic system by laser excitations. We can estimate the number of electron-hole excitations which were generated by absorbing $\hbar\omega = 1.5$ eV photons to $n\langle E \rangle / \hbar\omega = 0.06$/atom. This value is in good agreement with previous estimates [6]. Part of the deposited energy is transferred to other electron-hole excitations already during the duration of the laser pump pulse. The hottest electrons (≈ 1.5 eV above E_F) are known to decay within several fs [3], i.e., essentially within the laser pulse duration. This process increases *n* resulting in the observed values. Electron-hole scattering is also responsible for the thermalization of the hot electron distribution which is observed during the first 0.5 ps [18]. Thermalization is expected to occur faster for 3*d* than for 4*sp* electrons due to the stronger electron-electron interaction [18]. The hot electron thermalization time scale observed here is very similar to that measured for *sp* electrons in Au [19]. This is reasonable since unoccupied 3*d* states in Ni are confined to energies very close to E_F and the hot electrons reside mainly in delocalized *sp*-like states.

The quantities n/n_0 and also $n\langle E \rangle$ decrease monotonously above time delays of 0.15 ps. This is a clear indication that already on a sub ps time scale energy transfer from electron-hole recombinations to phonons sets in. Further evidence is provided by the rapid cooling down of the electronic system up to 2 ps (see open squares in Fig. 3). We note that during this time only the electrons are near thermal equilibrium but not the lattice due to the much slower atomic motion. Above 2 ps the electronic temperature varies only slowly. This suggests that electrons and lattice are now in thermal equilibrium. The energy transfer to phonons has, thus, heated up the lattice by about 70 K in agreement with rate equation modeling of similar experiments [7].

We now turn to the discussion of the fs spin dynamics. The size of the total exchange splitting which controls ferromagnetic order can be determined for such time delays where the electronic system has reached equilibrium. This is shown in the inset of Fig. 1. For the 1 ps symmetrized spectrum (*d*) the exchange splitting is clearly reduced to zero. At longer time delays such as 4 ps [spectrum (*e*)] the exchange splitting is almost completely reestablished. Below about 0.5 ps symmetrization fails since the electronic distribution function

deviates from a Fermi function and itself varies with time delay (see Fig. 2). Inspection of Fig. 1 shows that the majority spin peak shifts smoothly with time delay. It is plausible to assume that this allows us to observe how the exchange spitting is reduced (see Fig. 3). The different symbols in Fig. 3 (left part) show that this behavior is identical at different k points within the hole pocket near the L point of the Ni Brillouin zone.

The quenching of the Ni exchange splitting does not seem to be caused by a cooperative effect of a strong laser field and weak spin-orbit coupling as argued in Ref. [10]. A significant part of the exchange field reduction happens after the pump and probe laser pulses are in temporal overlap (see Fig. 3). A nearly instantaneous demagnetization while the pump laser field is on [10] can also be ruled out from Fig. 1. The majority peak position and, thus, the exchange field at zero time delay is unaltered compared to that before arrival of the laser pump pulse. This means no spin dynamics has occurred even if the laser field was strong enough to generate a significant amount of electron-hole excitations [see spectrum (*b*) in Fig. 2].

We can also rule out the transfer of a significant amount of angular momentum into the W(110) substrate by ballistic electron diffusion. Typical electron mean free paths during the first 300 fs are larger than the Ni layer thickness [20]. If a significant spin dependent electron transport would be effective during this time the quenching of the Ni exchange spitting should be much faster than observed.

Our measurements rather demonstrate that the laser induced demagnetization of Ni proceeds by energy transfer from hot electrons (holes) to low-energy spin excitations such as magnons and Stoner excitations. A repopulation of $\Delta n \approx 0.5$ majority spin electrons into minority spin states is required to quench the Ni magnetic moment by Stoner excitations. For transitions of the type $3d^{\uparrow} \rightarrow 3d^{\downarrow}$ at least the majority spin state binding energy of 180 meV (see Fig. 3) has to be overcome. This process would require a significant percentage of the total deposited energy. We estimate from the inset of Fig. 2 that during the first 0.5 ps only a total energy of about 60 meV/atom is transferred to phonons and spin excitations. It has been pointed out that transitions of the type $4sp^{\uparrow} \rightarrow 3d^{\downarrow}$ require much lower excitation energy [14]. The low density of $4sp$ states and the smaller spin-orbit coupling compared to $3d$ orbitals might explain the observed time constant of 300 fs. Stoner excitations can decay into magnons [21] over a ps time scale. This essentially causes a delocalization of the spin-flip excitations. On time scales below the spin-lattice relaxation time magnons are decoupled from the lattice [2] and can interact only with the electronic system. While the latter cools down via energy transfer to the lattice magnons can be reabsorbed leading to the restoration of the $3d$ exchange field. It is evident from Fig. 3 that this is not an instantaneous process. The electronic system initially cools down relatively fast (< 2 ps) but the Ni magnetism is reestablished with a longer time constant of 3.2 ± 0.2 ps.

In conclusion we have shown experimentally how the laser induced ultrafast demagnetization of single crystalline Ni films proceeds on an electronic level. The quenching of the Ni magnetic moment has been unambiguously measured for the first time by probing the $3d$ exchange splitting. Energy transfer between electronic and spin excitations is mediated by spin-orbit coupling. It takes place with time constants of 300 ± 70 fs and 3.2 ± 0.2 ps depending on the involved low-energy spin excitations such as Stoner pairs or magnons, respectively. It will be interesting to see a detailed theoretical model based on these results develop in the near future.

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