Ultrafast spin dynamics of magnetic metals in a nonequilibrium state

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The spin dynamics of magnetic metals like Ni, Fe in a nonequilibrium state is analyzed. The characteristic times for relaxation processes of the electrons, local magnetic moments, the magnetization and the time needed for reorientation of the magnetization are estimated. For illustration of the general analysis, results are presented for the magnetic response to hot electrons using magneto-optics.

Keywords: Spin dynamics; hot electrons

Se analiza la dinámica de los espines en metales magnéticos como Ni, Fe en un estado de no esquilibrio. Se estiman los tiempos característicos para procesos de relajación de los electrones, momentos magnéticos locales, la magnetización y el tiempo necesario para la reorientación de la magnetización. Para ilustrar el análisis general, se presentan los resultados para la respuesta magnética a electrones calientes usando magneto-óptica.

Descriptores: Dinámica de los espines; electrones calientes

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The study of nonequilibrium electronic states, for example optically by pump-probe experiments, is of increasing interest [1, 2]. For ferromagnetic transition metals like Ni, Fe etc., the response of magnetism to electronic excitations is important: How quickly do excited electrons thermalize [3, 4] and how quickly does magnetism, the magnetization and the direction of the magnetization change? [5, 6] For itinerant magnetism in transition metals, whose electronic structure is illustrated in Fig. 1, one expects on general physical grounds that the d-electrons and their magnetization respond on the same time scale, and that this response is material-specific.

The nonequilibrium electrons excited out of the exchange-split d-states in the Fermi sea will change the magnetization, since this depends generally on the electron distribution and since the effective Hubbard-type Coulomb interaction U and the exchange interaction J is changed in the nonequilibrium state. The thermalization of the excited non-thermal d-electrons together with the thermal ones in the Fermi sea constituting the hot magnetic moments will occur fairly rapidly of the order of several fs and a time scale much smaller than ps. Generally, the magnetic electrons have thermalized long before all electrons and electrons and lattice are again in equiblibrium. The time scale for this dynamics follows of course from the characteristic interactions U and J amongst the d-electrons, typically of the order of eV, and the magnetic moments at neighboring lattice sites. Note, changes of the magnetization must conserve angular momentum and this involves transfer of angular momentum between neighboring spins or between spins and electronic orbits (spin-orbit coupling). Schematically, the magnetic response to hot electrons shown in Figs. 1 and 2 is described by

$$\vec{M}[t_0] \rightarrow \vec{M}[n'_d(t), T_{\rm el}(t)] \rightarrow \vec{M}[T_{\rm el}(t)] \; . \qquad (1)$$

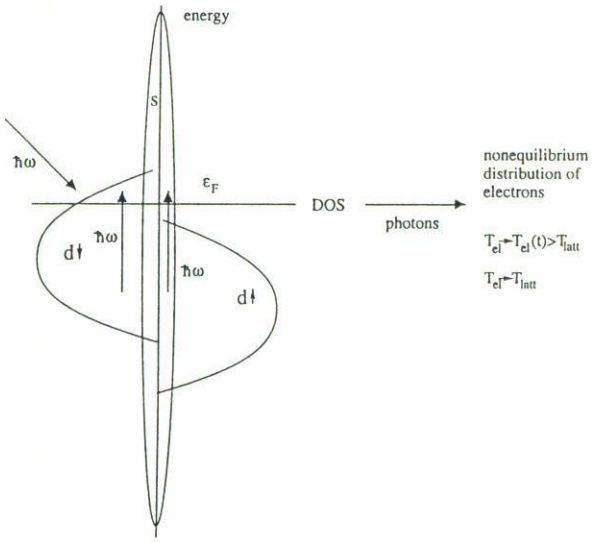

FIGURE 1. Schematic illustration of the density of states for ferromagnetic Ni, including spin-polarized d-states and unpolarized s-states. Photons excite s- and d-electrons into states above ε_F. No spin-flips occur. Since states are s-d-hybridized, electric dipole selection rules have to include this. Using the Hubbard Hamiltonian for the dynamics of the itinerant electrons, magnetism responds due to the interplay of the hopping integral t_{ij}, the intra-atomic Coulomb interaction U and the exchange coupling $J < U$. Note, for given $\hbar\omega$ one gets different number of spin up and down hot electrons due to differences in the initial DOS $N_\sigma(\varepsilon)$. Furthermore, the electron distribution $\{n_\sigma(\omega) + n_{-\sigma}(\omega)\}$ might change in time somewhat more slowly than $\{n_\sigma(\omega) - n_{-\sigma}(\omega)\}$.

Here, t_0 refers to the initial time at which the perturbation (of the pump laser, for example) has stopped, $n'_d(t)$ refers to the number of excited d-electrons which have not yet thermalized

at time t, and finally $T_{\rm el}(t)$ is the electron temperature which is different from $T_{\rm el}(t_0) = T_{\rm latt}(t_0)$ due to the thermalized hot electrons. Clearly, if the d-electons have thermalized again the magnetization is approximately given by $\vec{M}(T_{\rm el})$, where $T_{\rm el}$ is the electronic temperature and $T_{\rm el} \neq T_{\rm latt}$ in general. $T_{\rm latt}$ is the lattice temperature.

Since d- and s,p-electrons establish a common temperature $T_{\rm el}$ and since the s,p-electrons thermalize more slowly over a time scale of the order of fs to a few hundred fs generally [3], we expect the strongest non-equilibrium reduction of $M(T_{\rm el})$ when $T_{\rm el}$ is maximal. Note, the interplay of electron-electron interactions and electron-lattice interaction and diffusion of the hot electrons out of the region where the excitations occur determine at which time t one gets a maximal temperature $T_{\rm el}$.

It is important to realize that the hot electrons may cause disorder of the spin-directions of neighboring atoms on a time scale of the order of $t \sim J^{-1}$ as well as a change of the magnitude of the local magnetic moment due to an intra-atomic redistribution of the d-electron spins on a time scale of the order of $t \sim U^{-1}$. Generally, flipping locally a spin involves also a change of the magnitude of the moment [7, 8]. Using a more phenomenological picture, we may decompose the nonequilibrium magnetization as

$$M(t) = M^0(t) + M'(t) \,, \tag{2}$$

where $M^0(t)$ refers to the magnitude of the magnetization due to thermalized d-electrons at time t and $M'(t)$ to the spin-polarization of the nonthermal hot electrons. Clearly, the latter depends on the frequency ω of the light exciting the d-electrons out of the Fermi sea. Due to density of states effects and rapid spin-dependent interactions amongst the hot electrons, the magnetization of the nonequilibrium electrons

$$M'(t) \sim \left[n'_\uparrow(t) - n'_\downarrow(t)\right] \tag{3}$$

may cause $M^0(t)$ to be smaller or larger than the ground state magnetization at equilibrium. $n'_\sigma = n'_{d\sigma}$ refers to the nonthermal excited d-electrons with spin σ. If for given photon energy $\hbar\omega$ more majority-spin electrons are excited, then typically $M^0(t)$ has become smaller than the original thermal magnetization. Thus, one may expect for ultrashort response times (probe times in pump and probe experiments) that

$$M(n'_d = 0, T_{\rm el}) > M(n'_d \neq 0, T_{\rm el}) \,. \tag{4}$$

The changes of the direction of the long-range magnetization occur during much slower times of the order of 100 ps, since the magnetic anisotropy energy is typically much smaller than the exchange coupling J. Note, in the case of spin dynamics of cold spins in a warm lattice one expects a time scale of the order of 100 ps for the spin relaxation due to spin-orbit coupling [18]. The cold spins may occur due to very strong intra-atomic correlations amongst the electrons constituting the total spin.

We analyze now in more detail the time scales for the response of magnetism to nonequilibrium electrons. To treat the dynamics of itinerant magnetic transition metals within an electronic theory one may use, for example, the Hubbard Hamiltonian. Thus, one calculates the number of electrons at site i with spin σ

$$n_{i\sigma}(t) = \int d\varepsilon N_{i\sigma}(\varepsilon, t) f_\sigma(\varepsilon, t) \,, \tag{5}$$

where $N_{i\sigma}(\varepsilon, t)$ is the local density of states and $f_\sigma(\varepsilon, t) = f^0_\sigma(\varepsilon, T_{\rm el}) + \delta f_\sigma(\varepsilon, t)$ the distribution function to be determined with the help of the Boltzmann equation $\left[f^0_\sigma = (1 + e^{(\varepsilon_\sigma - \varepsilon_F)/kT})^{-1}\right]$. One gets approximately [3]

$$\delta f_\sigma(\varepsilon, t) = \delta f_\sigma(\varepsilon, 0) e^{-t/\tau_\sigma} \,, \tag{6}$$

with (neglecting for simplicity density of states effects)

$$\tau_\sigma = \tau_{0\sigma} \left[\varepsilon_F/(\varepsilon - \varepsilon_F)\right]^2 \tag{7}$$

as relaxation time for the electrons excited by $(\varepsilon - \varepsilon_F)$ above the Fermi energy ε_F. Here, (using for simplicity $\tau_{0\sigma} \simeq \tau_0$)

$$\tau_0 = \frac{64}{\pi^2\sqrt{3\pi}} \sqrt{\frac{m}{e^2 n}} = \frac{128}{\sqrt{3}\pi^2} \frac{1}{\omega_p} \,. \tag{8}$$

n is the number of electrons per atom and ω_p the plasmon frequency [9]. In accordance with Fermi's golden rule one has for the spin-dependent lifetime [2, 10]

$$\tau_\sigma \sim \frac{1}{N_\sigma(\varepsilon)} \,, \qquad \varepsilon \sim \varepsilon_F \,. \tag{9}$$

Evidently, these expressions describe that d-electrons have smaller lifetimes and therefore thermalize faster than s,p-electrons with smaller density of states (DOS) around ε_F for example. The d-electron thermalization speeds up as the DOS available at ε_F for the relaxing electrons increases [for Co, Fe: $\tau \sim 5 \to 10 \div 15$ fs for $(\varepsilon - \varepsilon_F) \to 0$] [1, 2]. Since $N_\uparrow(\varepsilon)/N_\downarrow(\varepsilon)$ varies for Ni, Co, Fe, Cr etc., one expects corresponding characteristic behavior of τ_σ or $\tau_\uparrow/\tau_\downarrow$, respectively. In the case of rapid spin flips of the hot electrons, one expects $\tau_\uparrow \simeq \tau_\downarrow$. Note, spin-flip collisions may cause excited electrons with spin σ to drop into holes in the $-\sigma$ d-band. In general, if the minority spin density of states $N_\downarrow(\varepsilon)$ is larger than $N_\uparrow(\varepsilon)$ around ε_F, then

$$\tau_\downarrow < \tau_\uparrow \,.$$

With increasing density of excitations, the lifetime τ shortens and then the thermalization will speed up. Also, according to the Boltzmann equation, τ shortens as the electronic temperature $T_{\rm el}$ increases

Using these equations and experimental results [2, 3], one estimates that the excited d-electrons thermalize approximately within a time range of 10–50 fs and establish a temperature $T_{\rm el}$. This is in accordance with the strong interaction U_{dd} amongst d-electrons which is of the order of a few eV. Also, note $U_{sd} > U_{ss}$, and $J \leq U_{dd}$ for example. Of course, it may take a time up to a few hundred fs until all s,p-type hot

electrons have thermalized [3]. Hence, the electron temperature $T_{\rm el}$ may increase with time after d-electrons thermalized, but s,p-electrons continue to thermalize. As time progresses ($t \to$ ps), the electron-lattice interaction described by $g_{\rm e-ph}$ becomes more active with respect to transferring energy from the electrons to the lattice and determines the time-dependent change of the electron temperature. thus, $T_{\rm el}$ decreases again. Approximately, $T_{\rm el}$ follows from [11]

$$C_{\rm el}(T_{\rm el})\frac{\partial T_{\rm el}}{\partial t} = -g_{\rm e-ph}(T_{\rm el} - T_{\rm latt}) + \frac{\partial}{\partial t}\int d\varepsilon\, \varepsilon\, N(\varepsilon)\delta f\ , \quad (10)$$

$$C_{\rm latt}(T_{\rm latt})\frac{\partial T_{\rm latt}}{\partial t} = g_{\rm e-ph}(T_{\rm el} - T_{\rm latt})\ , \quad (11)$$

where at time t_0 before the excitation by the laser electron and lattice temperatures are equal and $T_{\rm el} = T_{\rm latt} = T_0$. $C_{\rm el} = \partial E/\partial T$ is the electronic specific heat for the nonequilibrium state [12], $C_{\rm latt}$ is the lattice specific heat and δf the contribution to the electronic distribution function $f = f_0 + \delta f$ due to the nonthermal excited electrons [13]. Note, the interplay between distributing the excitation energy (input energy) over the s,p,d-electrons and the energy transfer to the colder lattice via the electron-lattice coupling $g_{\rm e-ph}$ determines $T_{\rm el}(t)$ and in particular the maximal temperature $T_{\rm el}^{\rm max}$ resulting for a given input photon energy. In general, in transition metals $g_{\rm e-ph}$ is larger for d-electrons than for s,p-electrons. As noted already, the temperature $T_{\rm el}(t)$ may continue to increase after most of the d-electrons responsible for magnetism have thermalized already, since the s,p-type hot electrons continue to thermalize.

The magnetic response to electronic excitations, in particular to d-electron excitations, is of course controlled by U and J, and possibly by spin-orbit coupling $V_{\rm so}$. Since $U_{dd} > U_{sd} > U_{ss}$, one expects an almost immediate weakening of the magnetization as d-electrons get excited (optically without spin flip) out of the exchange-split Fermi-sea into s,p-type states, see Fig. 1, [14]. As the d-electrons thermalize and feel the temperature $T_{\rm el}(t)$, one gets on general grounds

$$M(T_0) > M(t) \to M\left[T_{\rm el}(t)\right] \quad (12)$$

for the time-dependent response of the magnetization to excitations. Here, $M(T_0)$ is the magnetization at the temperature $T_0 = T_{\rm latt}$ at time t_0 before the excitations have increased the temperature. $M(t)$ refers to the magnetization during the time where nonthermal electrons reduce the magnetization. Of course, as the electrons relevant for magnetism reestablish a temperature $T_{\rm el}(t)$, one expects $M(t) \to M(T_{\rm el})$. Obviously, the magnetization will decrease until $T_{\rm el}^{\rm max}$ is reached and then recover again as $T_{\rm el}(t)$ decreases again. For $T_{\rm el} > T_C$, of course, $M \to 0$ and remains zero until $T_{\rm el}$ becomes again smaller than the Curie temperature T_C. This is illustrated in Fig. 2.

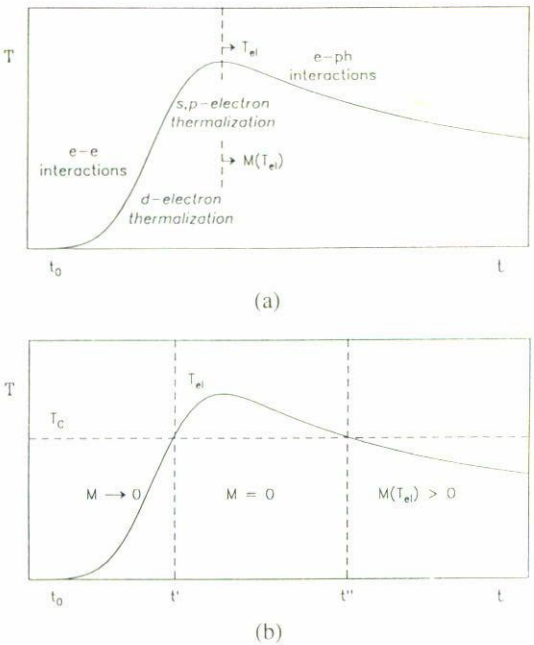

FIGURE 2. Illustration of the dynamics in Ni, for example, due to hot electrons, for a nonequilibrium state. t_0 is the time when excitation and subsequent relaxation and thermalization of the excited electrons begins. (a) Time dependence of the electron temperature $T_{\rm el}$ controlled by electron-electron and electron-lattice interactions. First d- and then s-electrons thermalize. $T_{\rm el}^{\rm max}$ reflects the interplay of the energy distribution over the progressively thermalizing electrons and energy transfer to the lattice. $M(t) = M(T_{\rm el})$ after electron thermalization. (b) If $T_{\rm el} > T_C$, T_C being the Curie temperature, then $M \to 0$ during the time $(t'' - t')$.

Using the Hubbard Hamiltonian or equivalently the Heisenberg Hamiltonian

$$H = \sum_{i,j} J\vec{\mu}_i \cdot \vec{\mu}_j\ , \quad (13)$$

where J is the exchange coupling between neighboring magnetic moments $\vec{\mu}_i$, one estimates for the ensemble of local magnetic moments μ_i a thermalization time of the order of

$$t \gtrsim \frac{1}{zJ\mu^2} \sim \frac{1}{T_C}\ . \quad (14)$$

Here, z is the number of nearest neighbors and typically $J \sim 0.1$ eV. Thus, for example, the magnetization of Fe should respond nearly twice as fast as the one of Ni. For Ni we estimate a response time to electronic excitations of the order of 100 fs or faster, dependent on the number of excitations and the excitation energy range $(\varepsilon - \varepsilon_F)$. Of course, changes of the magnetization must conserve angular momentum and this may involve not only (transversal) local spin excitations, but also the local intra-atomic-like spin-orbit coupling $V_{\rm so}$ ($V_{\rm so} \leq J$ for Ni, Fe) [15]. Note, if the nonequilibrium distribution causes also a decrease of μ_i, then the spin-relaxation time increases according to Eq. (14). For Ni, for example, μ_i may decrease by about 30% [8].

Within an electronic theory, the magnetization is approximately given by

$$M(t) \sim \left[n_\uparrow(t) - n_\downarrow(t)\right] , \tag{15}$$

with $n_\sigma(t) = \int d\varepsilon N_\sigma(\varepsilon) f_\sigma(\varepsilon, t)$ [16]. Clearly, this shows also that $\delta f_\sigma(t)$ and τ_σ determine the magnetic response to 'hot' electrons and that the electronic and magnetic response occur during the same time ($t \ll$ ps), the magnetic response being somewhat faster.

Of course, electronic excitations of d-electrons out of the Fermi-sea affect in general also the magnitude of the magnetic moments as is clear from

$$\mu_i(t) \sim \left[n_{i\uparrow}(t) - n_{i\downarrow}(t)\right] . \tag{16}$$

Note, however, the intra-atomic correlations amongs the d-electrons are of the order of $U \gg J$. Since in transition metals like Fe and Ni, the local magnetic moments exist above the Curie temperature T_c, one will generally observe a much weaker change of

$$\mu(t) = \mu\left[T_{\rm el}(t)\right]$$

due to $T_{\rm el}$. Note, for magnetism in Kondo systems the situation might be different. Then, hot electrons are expected to destroy the Kondo state if $T_{\rm el} \sim T_K$. T_K is the Kondo-temperature and of the order of the width of the DOS peak at ε_F.

Furthermore, the direction of the magnetization, $\vec{M}(t)$, will also change during a characteristic time in response to a perturbation. Since the direction of the magnetization is pinned to an easy crystal axis by the magnetic anisotropy energy $\Delta E_{\rm anis}$, which for transition metals is of the order of μeV, one estimates the response time

$$t \gtrsim \frac{1}{\Delta E_{\rm anis}} \tag{17}$$

for reorientation transitions of the magnetization. This gives a response time $t \sim 100$ ps for reorientations of the magnetization, for example at surfaces of films where the transition $M_\parallel \rightarrow M_\perp$ may be induced by an increase of the temperature [17]. Such a situation is illustrated in Fig. 3. Note, $\Delta E_{\rm anis}$ involves the spin-orbit or the spin-lattice coupling, respectively. The response of 'cold' spins in an excited warmer lattice is also controlled by the spin-lattice coupling and will occur during similar times $t \sim 50$–100 ps. This time has been calculated [18] and is observed [19].

This completes then the general discussion of characteristic times for the response of magnetism in transition metals to electronic excitations. One expects that the application of pump-probe spectroscopy to magneto-optics is particularly suited for studying the dynamics of magnetism. Therefore, we analyze in the following in detail the recent magneto-optical experiments observing the magnetic signal ΔI_- of the second-harmonic light (SHG) indicating a response of the magnetization in Ni to optically excited electrons much faster than 1 ps [6].

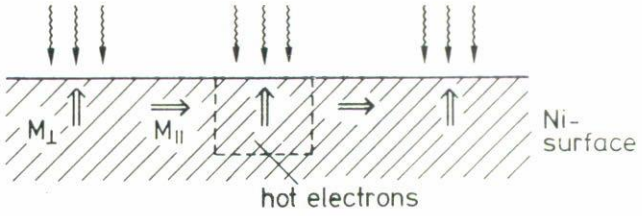

FIGURE 3. Light-induced magnetic pattern formation due to exciting hot electrons in Ni, for example. If in the irradiated regions the electronic temperature rises such that $T_{\rm el} > T_R$, then the parallel surface magnetization $M_\parallel$ changes at the temperature T_R to the perpendicular magnetization $M_\perp$. The reorientation transition $M_\parallel \rightarrow M_\perp$ is achieved by spin-orbit coupling and thus requires the time of the order of $t_{reor} \sim \Delta E^{-1}_{\rm anis}$. The cooling from $T_{\rm el} > T_R$ to $T_{\rm el} < T_R$ implies a further time delay.

The magnetic SH signal is given by

$$\Delta I_- \equiv I(\vec{M}, t) - I(-\vec{M}, t). \tag{18}$$

The SHG intensity $I(\vec{M}, t)$ is calculated by $I(2\omega) \propto |P(2\omega)|^2$, and the polarization is given in terms of the electric field by $P_i(2\omega) = \chi_{ij\ell} E_j E_\ell$ [20]. Since the second-harmonic generation intensity depends on $\vec{M}$ and $T_{\rm el}(t)$, one has $I(\vec{M}, T_{\rm el})$ [6]. Expanding the nonlinear susceptibility $\chi_{ijl}(\vec{M})$ into even and odd terms in M [6, 20], namely $\chi = \chi_{\rm e} + \chi_{\rm o}$, $\chi_{\rm o} \simeq \chi' M$, one gets ($I \propto |\chi|^2$) neglecting phase differences [21–23]

$$\Delta I_- \propto 4 \chi_e \chi' M. \tag{19}$$

Here, we assumed the approximation that mainly one tensor element of χ_{ijl} dominates. Similarly, we find for the quantity

$$\Delta I_+ \equiv I(\vec{M}, t) + I(-\vec{M}, t) \tag{20}$$

the result [6]

$$\Delta I_+ \propto |\chi_{\rm e}|^2 + |\chi'|^2 M^2. \tag{21}$$

Here, in general $M = M(t)$. For thermalized electrons and spins one may use in the equations for the magnetization $M = M(T_{\rm el})$. Then, for example,

$$\Delta I_- \propto A(T_{\rm el}) M(T_{\rm el}) . \tag{22}$$

The equilibrium magnetization for $T \equiv T_{\rm el}$ is approximated by $M(T) = M(T_0)\sqrt{1 - c(T - T_0)}$. The coefficient $A(T_{\rm el})$ includes Fresnel factors and magnetic anisotropy energy which also depend on $T_{\rm el}$ [besides on $T_{\rm el}$ via $M(T_{\rm el})$ [6]. Thus, ΔI_- exhibits more the magnetic dynamics and ΔI_+ reflects more directly the electronic temperature $T_{\rm el}$] [22]. This has been discussed previously by Hohlfeld *et al.* [6].

We calculate ΔI_- and ΔI_+ using Eqs. (18)–(22) and assuming for simplicity that the dominant dependence on $T_{\rm el}$ is due to $M(T_{\rm el})$. $\chi_{\rm e}(T, M)$ is expected to depend only weakly on temperature. The results of our calculations are compared with experiments on Ni by Hohlfeld *et al.* [6].

In Fig. 4 results are shown for the normalized change of the SHG signals

$$\delta_{\pm}(t) = \left[\Delta I_{\pm}(t) - \Delta I_{\pm}(t_0)\right]/\Delta I_{\pm}(t_0), \qquad (23)$$

where t_0 refers to the time at which $T_{\rm el}$ starts to increase initially above $T_{\rm latt}$ due to the probe-laser irradiation. Using the previous formulae, one gets approximately

$$\begin{aligned}\delta_{-}(t) &= -\left[1 - \Delta I_{-}(t)/\Delta I_{-}(t_0)\right] \\ &\simeq -\left[1 - \alpha(t) m(t)\right], \end{aligned} \qquad (24)$$

with $\alpha(t) = [\chi_{\rm e}(t)\chi'(t)]\,/\,[\chi_{\rm e}(t_0)\chi'(t_0)]$ and $m(t) = M(t)/M(t_0)$. Similarly, we find for $\delta_{+}(t)$

$$\begin{aligned}\delta_{+}(t) &= -\left[1 - \Delta I_{+}(t)/\Delta I_{+}(t_0)\right] \\ &\simeq -\left[1 - \frac{|\chi_{\rm e}(t)|^2 + |\chi'(t)|^2 M^2(t)}{|\chi_{\rm e}(t_0)|^2 + |\chi'(t_0)|^2 M^2(t_0)}\right]. \end{aligned} \qquad (25)$$

Note, neglecting for simplicity the temperature dependence of $\chi_{\rm e}$ and χ', one obtains $\chi_{\rm e}(t) \simeq \chi_{\rm e}(t_0)$ and $\alpha \simeq 1$ [22]. This simplification is made in the calculations shown in Fig. 4. Previous results for SHG yielded $\chi_{\rm e} \sim \chi_{\rm o}$. $\chi_{\rm e}$ and $\chi_{\rm o}$ can be determined somewhat independently by changing the polarization of the SHG [25].

Fig. 4a shows results for $T_{\rm el}(t)$. Using these results for $T_{\rm el}(t)$ and $M = M(T_{\rm el})$, we get the results for $\delta_{-}(t)$ shown in Fig. 4b. In Fig. 4c, results for $\delta_{+}(t)$ are shown.

For calculating $T_{\rm el}$ we use Eq. (10), taking into account the finite width of the exciting laser pulse [26]. Due to the finite width of the pump laser pulse, we estimate that $T_{\rm el}(t)$ becomes maximal at $t \sim 200$ fs and thus δ_{-} minimal at this time. For a pump laser pulse of smaller width, of course, $T_{\rm el}(t)$ becomes maximal at shorter times, possibly $t \leq 100$ fs. Indeed, recent experiments by Hohlfeld *et al.* indicate such a behavior [25]. However, note the time at which $T_{\rm el}(t)$ becomes maximal is set by the interplay of the heat put into the electronic system by the pump laser and the heat loss to the lattice mediated by the electron-lattice coupling. For a delta-function like pump we estimate for transition metals times of the order of $t \sim g_{\rm ep}^{-1}$ when $T_{\rm el}(t)$ is maximal.

The simple theory using $M = M(T_{\rm el})$ and a temperature independent ratio $b = |\chi'|M(t_0)/|\chi_e|$ is in overall fair agreement with experiment (Fig. 4). The rapid decrease of $\delta_{-}(t)$ is due to the decrease of $M(t)$ caused by the increase of $T_{\rm el}$ due to the hot electrons. After reaching a minimum the quantity $\delta_{-}(t)$ increases again, since $M(t)$ increases again, see $T_{\rm el}$ and $T_{\rm el} \to T_{\rm latt}$. Note, the lattice will be somewhat warmer at the time $t \sim$ ps than at the time t_0 and hence $\delta_{-}(t)$ and $\delta_{+}(t)$ approach a value which is smaller than the one at t_0. $T_{\rm el}(t)$ refers to Ni with $T_{\rm el}^{\rm max} \simeq 580$ K, $T_{\rm el}(t_0) = T_{\rm latt} \simeq 350$ K and $T_{\rm latt} \simeq T_{\rm el} = 450$ K at $t \gtrsim 2$ ps [6].

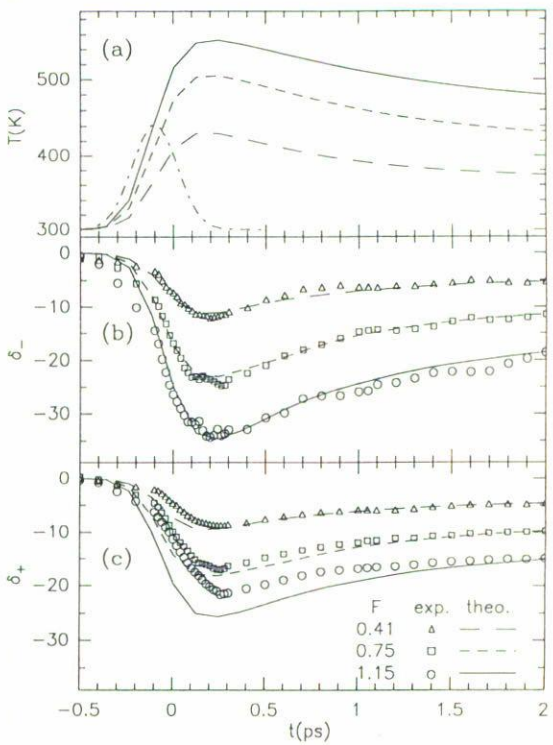

FIGURE 4. Illustration of the short-time behavior of the electronic temperature in panel (a) and the SHG magnetic contrast signal $\delta_{-}(t) = (\Delta I_{-}(t) - \Delta I_{-}(t_0))/\Delta I_{-}(t_0)$ in panel (b) and of $\delta_{+}(t) = (\Delta I_{+}(t) - \Delta I_{+}(t_0))/\Delta I_{+}(t_0)$ in panel (c). For the electronic temperature $T_{\rm el}(t)$ in panel (a) we use results obtained from Eq. (10). The center of the gaussian pump laser pulse is set at $t = -100$ fs. This is indicated in panel (a) by the dash-dotted line representing the puls shape (in arbitrary units). t_0 refers to the time before the onset of the pump pulse. The results for the SHG signal were calculated using Eqs. (24) and (25) and are compared with experimental data [6]. F refers to the laser fluence normalized to 6 mJ/cm^2. $M(t)$ is calculated from $M(T_{\rm el})$.

Note, for $\alpha \simeq 1$ in our approximate formulae Eqs. (24) and (25) only δ_{+} is affected by the temperature dependence of χ' and $\chi_{\rm e}$. Interestingly, the calculated values for δ_{+} at the minimum are too negative suggesting that $\Delta I_{+}(t)$ and hence $\chi_{\rm e}(t)$ may increase somewhat for increasing temperature and may not be constant as assumed. One gets for Ni with $T_{\rm latt}(t_0) \simeq 350$ K and $T_{\rm el}^{\rm max} \simeq 580$ K that $T_{\rm latt}(t \gtrsim$ ps$) \simeq$ 450 K. Then we estimate that $\delta_{-}(t)$ is lower by 0.05 at times $t \sim$ ps and that $\delta_{-} \simeq M(t_{\rm min})/M(t_0) - 1 \approx -0.3$ at the minimum. Experimentally one observes $\delta_{-} \simeq 0.02 - 0.03$ at $t \sim$ ps and $\delta_{-} \simeq 0.34$ at the minimum. For later times $t > t_{\rm min}$, when the electronic temperature approaches the lattice temperature $T_{\rm latt}$ ($T_{\rm el} \longrightarrow T_{\rm latt}$), the formula $\Delta I_{-} \propto M(T_{\rm el})$ describes satisfactorily experiment. Note, δ_{-} for times $t \sim$ (ps) is somewhat smaller than $\delta_{-}(t_0)$ due to the warming up of the lattice by the hot electrons. Also the simple theory predicts for longer times correctly [6]

$$\frac{\Delta I_{-}}{\Delta I_{+}} = \frac{\chi_{\rm e}\chi'}{|\chi_{\rm e}|^2 + |\chi'|^2 M^2} M \propto M.$$

While experiments and theory are in overall fair agreement, one expects on general grounds that $\delta_{\pm}(t)$ may decrease at very short times $t < t_{\min}$ faster than $\delta_{\pm}[M(T_{\rm el})]$ calculated using the equilibrium values $M(T_{\rm el})$ for the magnetization. This is expected to result from the fact that at ultrashort times the electrons have not yet all thermalized and that dependent on the photon energy $\hbar\omega$ one probes optically essentially the smaller magnetization $M^0(t)$ of the thermalized electrons, see Eq. (2). Of course, $\delta_{\pm}(t) \to \delta_{\pm}[M(T_{\rm el})]$ for increasing times as more and more hot electrons have thermalized.

Further studies, including the determination of the dependence of the dynamics on light frequency $\hbar\omega$, are necessary. This might reveal interesting band-structure effects for Ni, Fe and Co, for example [24].

This demonstrates how the dynamics of magnetic transition metals at nonequilibrium can be studied using nonlinear SH and magneto-optics. These experiments support the general theory for the dynamics of magnetism in transition metals discussed by Eqs. (1)–(12). One may conclude generally that ultrashort magnetic response, spin relaxation of transition metals at nonequilibrium may occur during times of the order of 10–50 fs and long before lattice and electrons have reached equilibrium again.

Note, for rare-earth metals in contrast to transition metals the f-electrons constituting the spins may be treated as a separate system coupled to the s,d-electrons which get excited. Then, exchange J and spin-orbit interaction $V_{\rm so}$ are larger and one may find for nonequilibrium the situation $T_{\rm el} \neq T_s(t)$, where T_s refers to the local spins of the rare-earth atoms, and furthermore that both $T_{\rm el}$ and T_s are different from $T_{\rm latt}$ [11].

In conclusion, we have identified characteristic times for the short-time dynamics of magnetic metals not at equilibrium due to hot electrons. At times $t \gtrsim$ ps, the spin dynamics may occur for 'cold spins' in an excited warmer lattice. Then the spin-lattice coupling will play an important role for spin relaxation processes occuring on a time scale of approximately $t \sim 100$ ps [18].

It would be interesting to analyze also the dynamics of the many-body Kondo singlet state and of magnetism in heavy-Fermion systems. The dynamics of the Kondo state is expected to be characterized by the time $t \sim 1/T_K$, where T_K is the Kondo temperature. Hot electrons will destroy the singlet state if $T_{\rm el} > T_K$. Similarly, for heavy Fermions the nonequilibrium hof electrons raising $T_{\rm el}$ will destroy the resonance-like DOS peak at ε_F and thus typical magnetic effects. Again changes occur during a time $t \sim U_{\rm eff}^{-1}$, where $U_{\rm eff}$ is the effective electron correlation responsible for the narrow band of width w and $T_{\rm el} > w$ should destroy the heavy-Fermion characteristics. Finally, it would be interesting to study systems where $V_{\rm so}$ controls angular-momentum conservation and thus the magnetic dynamics.

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9. One gets these results using Fermi-liquid theory or the random-phase approximation (RPA) if $(\varepsilon - \varepsilon_F) \ll \varepsilon_F$.

10. The usual collision integral expression gives for an energy transfer $\Delta\varepsilon = \varepsilon - \varepsilon'$ the result $\tau_\sigma^{-1}(\varepsilon) \propto \int_o^\varepsilon d\varepsilon' \int_{-\Delta\varepsilon}^o d\varepsilon'' N_\sigma(\varepsilon')\{N_\sigma(\varepsilon'')N_\sigma(\varepsilon''+\Delta\varepsilon)\cdots\}$. Here, matrix-element effects are neglected and we assume that the relaxation process involves no spin flips. This collision integral describes the scattering process $\varepsilon \to \varepsilon'$ and $\varepsilon'' \to \varepsilon'' + \Delta\varepsilon$ of two electrons. Hence, approximately $\tau_\sigma(\varepsilon) \propto N_\sigma^{-1}(\varepsilon - \Delta\varepsilon)$ in accordance with Fermi's golden rule. Note, the collision integral involves at finite temperatures in general the Fermi-function factors $f_i(1-f_i)$, $i = 1, 2$, for the two interacting electrons. Thus, one finds $\tau_\sigma = \tau_\sigma(t)$ for thermalizing electrons.

11. The time dependence of $T_{\rm el}(t)$ may be determined approximately also by using the master equations $c_{\rm el}\dot{T}_{\rm el} = -\alpha_1(T_{\rm el} - T_{\rm latt}) - \alpha_2(T_{\rm el} - T_\mu) + p(t)$ for the electrons, $c_\mu \dot{T}_\mu = -\alpha_2(T_\mu - T_{\rm el}) - \alpha_3(T_\mu - T_{\rm latt})$ for the spins, and $c_{\rm latt}\dot{T} = -\alpha_1(T_{\rm latt} - T_{\rm el}) - \alpha_3(T_{\rm latt} - T_\mu)$. Here, $c_{\rm el}$, c_μ and $c_{\rm latt}$ denote the specific heat, p is the laser power and α_i are constants. If diffusion is important, then $c_{\rm el}\dot{T}_{\rm el} = \frac{\partial}{\partial z}(K_{\rm el}\frac{\partial}{\partial z}T_{\rm el}) + \cdots$, where $K_{\rm el}$ is the thermal diffusion coefficient of the electrons. $T_{\rm el}^{\max}(t)$ will be generally determined by the interplay of the electron-electron and the electron-lattice interaction. Note, for itinerant transition metals it is not strictly valid to separate the conduction electrons from those constituting the magnetic moments.

12. Note, $c(T_{\rm el})$ is generally not equal to the equilibrium state specific heat.

13. The function $f(\varepsilon,t)$ may be determined by using the Boltzmann equation $\partial\delta f/\partial t \simeq \frac{1}{\tau}\delta f$, see Ref. 3, or by using the Liouville equation for the density $\rho(t)$ and $i\hbar\dot{\rho} = \langle[H,\rho]\rangle$.

14. Here, we do not consider situations where the exchange interaction increases due to excitations as may be the case for some magnetic semiconductors.

15. $V_{so} \approx 40$ meV for Ni, $V_{so} \approx 70$ meV for Fe, for example.

16. The magnetization is approximately given within a Ising-like model by $M \sim (c_+\mu_+ - c_-\mu_-)$, where c_+ is the probability to find a magnetic moment μ_+ pointing in the direction of the magnetization and c_- and μ_- are correspondingly defined. Generally, $\mu_+ \neq \mu_-$ and perturbations cause changes $\mu_+ \rightarrow \mu_-$, for example, and thus a decrease of M due to directional disorder as well as due to a decrease in the magnitude of the magnetic moments.

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20. The susceptibility tensor $\chi_{ij\ell}(\vec{M})$ may be expanded into even and odd terms in $\vec{M}$, see U. Pustogowa, W. Hübner, and K.H. Bennemann: *Phys. Rev. B* **48** (1993) 8607. Nearly equivalently one may write $\chi_{ijl}(\vec{M}) = \chi_{ijl}(0) + \chi_{ijlk}M_k + \cdots$. It is then straightforward to get $\Delta I_- \propto M$.

21. Note, for simplicity the phase between χ_e and χ_o has been neglected. Also we have assumed for simplicity that one tensor element dominates in χ_{ijl}. If analyzing the polarization dependence of SHG and its time evolution one must of course use $\chi_{ijl}(\vec{M})$.

22. Approximately $\Delta I_+ \propto |\chi_e(T)|^2(1 + aM^2)$, with $a(t) = |\chi'|^2/|\chi_e|^2$, $\chi' \equiv \chi_{ijkl}$. Hence, ΔI_+ varies with $M^2(T_{el})$, since the temperature dependence of $\chi_e(T)$ and a is expected to be weaker. Note, the SH intensity I involves Fresnel coefficients which are temperature dependent, see T. Luce, W. Hübner, and K.H. Bennemann, *Z. Phys. B* **102** (1997) 223.

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24. Fig. 1 suggests that the magnetic response may depend on the excitation energy $\hbar\omega$ and may reveal interesting effects due to the structure in the DOS $N_\sigma(\varepsilon)$. For example, one could excite using circularly polarized light mainly electrons in the minority band and thus possibly for very short times enhance magnetism until thermalization yields $M(T_{el})$ with $T_{el} > T_{latt}$.

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26. In the calculation of the electron temperature using Eq. (10), we use the following parameters. The nonequibilbrium electron distribution is created by the pump laser, modelled by a Gaussian pulse shape of width 280 fs (FWHM). The center of the pulse is set to $t = -100$ fs in order to best describe the onset and slope of the reduction in the signal as observed in the experiment. For the decay of the nonequilibrium electron distribution, we use Eqs. (6) and (7) with $\tau_0\ \varepsilon_F^2 = 25$ fs eV^2. The lattice specific heat is taken to be constant, $c_{latt} = 3.6 \times 10^6 \mathrm{Jm^{-3}K^{-1}}$, the electronic specific heat is parametrized to have the temperature dependence as calculated in [27], but its value is scaled by a factor of 4.5 in order to obtain results for the final electron and lattice temperatures in agreement with the experimental observations. This leads to a value of $c_{el}(T_{el} = 300\mathrm{K}) = 1.4 \times 10^6 \mathrm{Jm^{-3}K^{-1}}$. The value of the electron-phonon coupling constant used is $g_{e-ph} = 2 \times 10^{18}\ \mathrm{Wm^{-3}K^{-1}}$.

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