Ultrafast Spin Dynamics of Ferromagnetic Thin Films Observed by fs Spin-Resolved Two-Photon Photoemission

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Using a "pump and probe" technique, the time scale of spin relaxation effects in ferromagnetic thin films is investigated. Samples are excited by a 3 eV "pump" laser pulse ($\tau \approx 170$ fs), and electrons are photoemitted by a 6 eV "probe" pulse, after delays ranging up to 1 ns. The spin polarization of the photoelectrons is measured using a Mott detector. The time dependence of the spin polarization of thin Ni films on Ag is explained in a local magnetic moment picture with two excitation processes. Stoner excitations are responsible for the reduction of the observed spin polarization on a time scale of 1 ps and phonon-magnon scattering leads to the loss of long range magnetic order on a time scale of 500 ps. [S0031-9007(97)04890-4]

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The interactions between quasiparticles like electron-electron, electron-phonon, and electron-magnon scattering determine the macroscopic properties of matter at finite temperatures, and the dynamical response to external excitations; also properties like superconductivity and giant magnetoresistance are governed by them. Experimentally these interactions are reflected by the lifetime broadening of spectroscopic features. If these interactions are specifically included in the interpretation of experimental results, then they are usually treated as instantaneous, meaning that the system under consideration is always in thermodynamical equilibrium, whereby the true dynamics of these processes is neglected.

The magnetism of transition metals at finite temperatures is one of the most challenging topics in modern physics and much work has been done to calculate thermodynamic properties like the magnetization M, the susceptibility χ, and the Curie temperature T_C from first principles. An itinerant ferromagnet shows two types of magnetic excitations. Magnons which follow an approximately quadratic dispersion law are responsible for the low and medium temperature properties, whereas single particle excitations, the Stoner excitations, cost much more energy. Early models either neglected spin fluctuations (Stoner model) and thus predicted much too high Curie temperatures, or neglected the itinerant character leading to a Heisenberg-like description. Modern theories combine both pictures. A Stoner-type intinerant part leads to the formation of local moments and a Heisenberg-like part describes their interaction [1,2]. We will show in this Letter that both kinds of magnetic excitations are important to understand the dynamics of transition metal ferromagnets.

An experimental approach to investigate these interactions within a real-time experiment is very difficult, because a time resolution on the time scale of the electron-electron scattering ($\sim$fs) has to be achieved [3–7]. In the last few years these time scales became accessible by the development of commercial laser systems generating ultrashort pulses. These laser systems are most prominently applied in investigating electron scattering dynamics in semiconductors due to the industrial interest in high frequency devices [8–11]. The knowledge about scattering dynamics in ferromagnetic metals, however, is still quite poor and sometimes contradictory. These experiments are usually done by exciting the electron gas by a short laser pulse and probing the system with a second pulse after well defined delay times. In a first time resolved two-photon photoemission experiment, with a several ns long, medium intensity heating pulse, Vaterlaus *et al.* determined the magnetization relaxation time in Gd to 100 ± 80 ps [12,13] and could restrict the relaxation times in Fe to about 30 ps–20 ns, which is also 2 orders of magnitude larger than the electron relaxation times. The relaxation time in Ni was estimated by Agranat *et al.* to about 1 ns [14].

Conceptually, the reaction of a metal upon an external perturbation, such as laser heating, is usually treated by consideration of the energy transfer between two subsystems: the electron gas and the atomic lattice [15,16]. This is motivated by the observation of different excitation processes for each subsystem. The reaction of the whole system upon an external perturbation is then governed by the internal relaxation of each subsystem and its interaction with the others. In case of ferromagnets, the electronic subsystem is further split into a pure magnetic and an electronic one. Such a separation seems to be justified by the observation of an extremely long relaxation time of the magnetization compared to electron-electron and electron-phonon relaxation times, which both are in the sub-ps to ps regime [3–7]. As mentioned above, magnons are responsible for the medium temperature properties of transition metal ferromagnets. The energy transfer is therefore most likely caused by the phonon-magnon interaction. The electron-electron relaxation is governed by the Coulomb interaction. The coupling of the electron

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spins to the lattice is mediated by the much weaker spin-orbit coupling thus explaining the longer spin-lattice interaction time.

In more recent experiments by Beaurepaire *et al.* [16], as well as by Hohlfeld *et al.* [17], using fs heating pulses, however, a fast demagnetization of Ni films upon laser heating on a time scale of about 1 ps was reported, seemingly contradicting the early observations of Vaterlaus *et al.* It is the intention of this Letter to resolve these contradictions experimentally by covering both time scales within a single experiment, and additionally to outline a possible explanation by carefully analyzing the models describing the electronic and magnetic subsystems, as well as the interactions between these systems.

In entering a new experimental field, like time resolved spectroscopy on ferromagnetic systems it is essential to apply different experimental methods to avoid confusion by features intrinsically related to the spectroscopic method. In two recent experiments the magnetic relaxation was investigated by using the Kerr effect [16] and the second harmonic generation [17]. Here we report on the first use of time resolved, spin polarized photoemission with fs time resolution, using a two photon photoemission setup, covering relaxation times from below 1 ps up to 1 ns. Spin polarized photoemission is extensively used in investigating magnetic materials since it is a method which can be most directly related to the sample magnetization. In the adiabatic limit the relative change of the measured polarization of the photoelectrons upon temperature reflects the change of the sample magnetization. In a time resolved experiment using short laser heating pulses, however, special care has to be used in relating spectroscopic results to thermal equilibrium properties like the magnetization, especially for short delay times, when the system has not reached equilibrium. A second method, also with direct access to the sample magnetization, is the Kerr effect, applied in [16]. This method however is exclusively bulk sensitive, whereas the photoemission escape depth can be tuned by the photon energy. Second harmonic generation, applied in [17], is exclusively surface and interface sensitive and additionally, the magnetic information is contained more indirectly in the nonlinear susceptibility. All methods are influenced by changes in the electronic population, which has to be taken into account especially for short delay times. After a short description of our experimental setup we discuss the time dependent spin polarization of thin Ni films observed after laser heating and compare it to time scales observed for other ferromagnetic and nonmagnetic materials.

As a primary excitation source we use a Ti:Al_2O_3 laser system with a pulsed output of 4 μJ/pulse, a photon energy of 1.5 eV, and a pulse width of 170 fs. In a first step the photon energy is doubled to 3 eV and then the beam is split. One of the beams is used as the "pump" beam, to heat the sample. The optical path length of the second beam can be varied with respect to the heating beam by an optical delay line. The frequency of the "probe" pulse is doubled again to a photon energy of 6 eV, so that single photon photoemission is possible. Both beams are then focused to the same point of the sample, with a diameter of about 200 μm. Photoelectrons, excited by the 6 eV probe pulse, are spin analyzed by a Mini-Mott detector with a polarization efficiency $S_{\text{eff}} = 0.12 \pm 0.02$. The experimental setup is schematically shown in Fig. 1. Thin Ni films on Ag(100) are grown at room temperature by electron beam evaporation from a high purity Ni rod. Ni was chosen because of its high spin polarization of the photoemitted electrons, which is above 30% at the probe energy of 6 eV [18]. As for all magnetic thin film systems, the Curie temperature of the Ni overlayer can be varied by growing films of different thicknesses [19]. The incident light was *s* polarized; thus dicroic effects are not expected. The sample was remanently magnetized.

Figure 2 shows the normalized spin polarization of the photoemitted electrons for two film thicknesses as function of the delay time between heating pulse and probe pulse. The thinner film, 6 Å thick, has a Curie temperature of approximately 360 K, the thicker one, 12 Å thick, of approximately 480 K. The spin polarization has been normalized for negative delay times, when the probe pulse precedes the heating pulse. A background asymmetry, caused by instrumental asymmetries of the spin detector, as well as by electrons which are photoemitted in a two-photon process from the heating pulse, is subtracted.

The general behavior of the spin polarization vs delay time reveals the same characteristic features for both film thicknesses. At short delay times the polarization exhibits a very steep drop, followed by a slower decrease for longer delay times. The width of the fast, steplike decrease at time zero (Fig. 3) reflects the laser pulse width. Therefore the relaxation time for this fast demagnetization process has to be below 300 fs. The change in slope

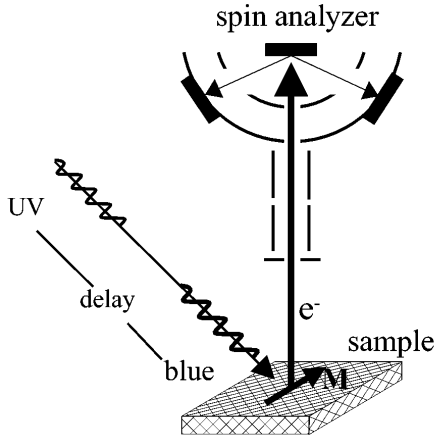

FIG. 1. Experimental setup: the pump pulse first heats the sample. After a variable delay time, electrons are photoemitted by the probe pulse, and the spin polarization is measured in a Mini-Mott detector.

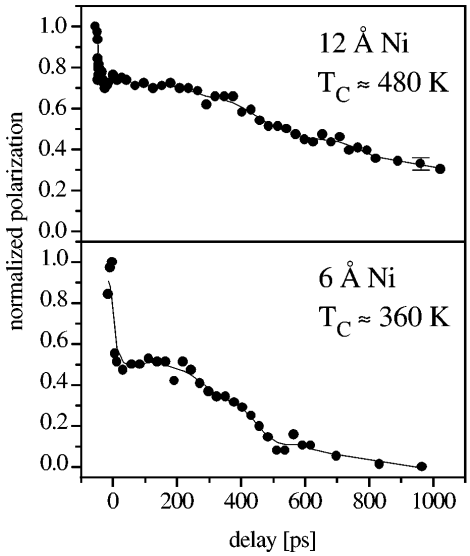

FIG. 2. Normalized spin polarization of the photemitted electrons vs delay time for Ni films with different Curie temperatures. Solid line: guide to the eye; error bar: statistical error.

at 500 ps for the 6 Å film indicates that the spin degrees of freedom have reached the macroscopic Curie temperature which is equivalent to the observation that the long range magnetic order is destroyed. Thus magnetic relaxation times within the subpicosecond range as well as in the nanosecond range are observed in a single experiment. This shows that the recent observation of short relaxation times in Ni [16,17] does not contradict the results of Vaterlaus *et al.* For the thicker film, which has a substantially higher Curie temperature, this temperature is not reached up to a delay time of 1 ns but the short time relaxation process is also present. There are some additional points to be mentioned before we will outline a model including both relaxation times. Both relaxation processes depend on the macroscopic Curie temperature. This is obvious for the long time relaxation since the Curie temperature has not been reached up to 1 ns for the thicker film. But also for the short time process

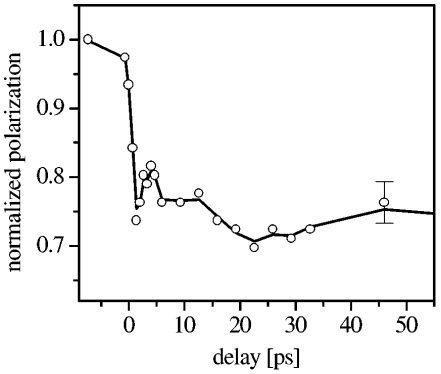

FIG. 3. Normalized spin polarization near time zero on an expanded time scale for the 12 Å thick Ni film.

the decrease in polarization is smaller for the thicker film with the higher Curie temperature. The depolarization at short delay times is not complete, although the equilibrium temperature, especially for the thin film is above the macroscopic Curie temperature. The polarization partially recovers after about 50 ps. Finally, the short relaxation time is of the order of electron thermalization times and thus should be related to the temperature of the electronic subsystem. Additionally near the time zero the main features of the spectrum reflect the change in the occupation of the electronic states (Fig. 3). Because of the density of states of Ni, hot electrons have mostly minority character. Thus the change in spin polarization reflects both the existence of magnetic excitations and the presence of "hot electrons" until electrons are thermalized.

The measured change in spin polarization is now explained as follows: After exciting the electron gas by a short laser pulse it relaxes into thermal equilibrium on a time scale of some ten femtoseconds. On the same time scale Stoner excitations are created by electron-electron scattering leading to a reduced local moment. This reduction is related to the equilibrium temperature of the electron gas and the local moment is not expected to vanish as long as the electron temperature does not approach the Stoner or mean field Curie temperature of some thousand degrees. This explains the incomplete demagnetization at short delay times. In this time domain, the development of the spin polarization is governed by the high electronic temperature. The thermalization of the electron gas with the lattice decreases the electron temperature and thus leads to a small partial recovery of the local moment. This happens on a time scale of some ps. The complete demagnetization of the sample on a time scale of some hundred ps is subsequently related to the creation of magnons within the magnetic subsystem by phonon-magnon interaction. A direct electron-magnon excitation cannot be excluded but a relaxation time of the same order as for the electron-phonon relaxation would be expected. By this time, the spin system itself approaches the higher electron and lattice temperatures. The magnetization follows this development until either the Curie temperature is reached or all heat baths are in thermodynamic equilibrium [20]. Thus we relate the short time demagnetization to the excitation of Stoner pairs (or more generally to longitudinal spin fluctuations) and the long time demagnetization to the excitation of spin waves (or transversal spin fluctuations). Nevertheless the extremely long relaxation time for spin-wave excitation of several hundred ps is astonishing and should be further investigated in the future.

Effectively this model of the processes corresponds to a separation of the total system into an electronic and a magnetic subsystem. While this approach is accepted for rare earth systems, which exhibit well localized $4f$ electrons separated from the conduction electrons, it might be questionable in the cases of Fe, Co, and Ni. For these

itinerant ferromagnets the band structure is intrinsically related to the occurrence of the magnetic moment. The driving force for the existence of a magnetic moment in these materials is the strong intra-atomic exchange interaction leading to an exchange split band structure and thus to a magnetic moment. This intra-atomic exchange interaction cannot be separated from the electronic subsystem. The interatomic exchange interaction between local moments, however, may be separated, since it does not affect the local electronic structure within a first order approximation. Thus one ends up with a Stoner-like model for the electronic subsystem and an effective Heisenberg model for the long range magnetic order. The elementary excitations are Stoner excitations and spin waves, respectively. The coupling between the subsystems may then be described by a coupled set of macroscopic thermal diffusion equations containing the specific heats of each subsystem as described by Beaurepaire *et al.* The specific heat due to Stoner excitations contributes to the electronic specific heat, and the magnon specific heat which is experimentally accessible in caloric measurements represents the magnetic specific heat. This is effectively what we have used in our description of the time dependent magnetic relaxation phenomena.

Summarizing our results, we observe two different demagnetization processes on two different time scales using time dependent photoelectron spectroscopy with spin analysis. One is a very fast process on a sub-ps time scale, probably due to an excitation of Stoner pairs by the hot electrons gas. The second, slow process is readily attributed to the spin-lattice interaction on a time scale of a few hundred ps. The observed decrease of the magnetization is dependent on the Curie temperature of the film and the total laser power absorbed in the pump process. Additionally we have outlined a model description based upon the three subsystem model. We observe however that the local magnetic moment cannot be decoupled from the electronic subsystem in the case of itinerant ferromagnets. This leads to the attribution of the fast demagnetization process to Stoner pair excitations on the time scale of the electron-electron relaxation. As a consequence of this, we expect the short time demagnetization to be nearly absent in the case of iron, since its local moment hardly changes even far above the macroscopic Curie temperature.

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[20] Fundamentally, the concept of temperature is only then well defined, if a system has reached thermodynamic equilibrium. The internal energy redistribution has to be faster than external interactions. This clearly applies to the electronic subsystem after some hundred fs and the lattice after some ps. For the spins it depends on the speed of the magnon-magnon interaction, which is not possible to determine in this experiment. Without a well defined temperature the state of a system has to be described by occupation numbers.