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Magnetization dynamics of Ni and Co films on Cu(001) and of bulk nickel surfaces

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The ultrafast magnetization dynamics of thin Ni and Co films on Cu(001) and of polycrystalline Ni surfaces was studied by pump-probe reflection second-harmonic generation, utilizing 150 fs/800 nm laser pulses. In all cases no delay between electron excitation and magnetization breakdown was observed within the experimental time resolution. An upper limit of such delay is 50 fs in case of bulk Ni surfaces. The recovery of magnetization follows the electron temperature relaxation during the first few picoseconds and thereafter cooling by regular thermal diffusion. [S0163-1829(99)50510-9]

Ultrafast spin dynamics of itinerant ferromagnets following optical excitation is presently a highly controversial topic due to three contradicting reports[1–3] on electron and spin relaxation in Ni. In all three cases pump-probe experiments were carried out on Ni samples of different thicknesses in various environments, employing different detection schemes. It is the purpose of this work to present new results which help to clarify the situation.

Beaurepaire *et al.*[1] used 60 fs/620 nm laser pulses to measure both the transient transmissivity and the linear magneto-optical Kerr effect (MOKE) of 22 nm Ni films protected by a MgF_2 coating. The electron thermalization time was found to be 260 fs with an electron temperature decay constant of 1 ps. In contrast, the spin temperature deduced from the time dependence of hysteresis loops rose during the first picosecond reaching its maximum around 2 ps. On this basis the authors postulated different electron and spin dynamics. The investigation was done at a fixed pump fluence, i.e., for only one initial electron temperature.

Hohlfeld *et al.*[2] carried out pump-probe reflection second-harmonic generation (SHG) with 150 fs/800 nm pulses on magnetized polycrystalline bulk Ni in air, assuming that SHG monitors the surface magnetization of Ni undisturbed by the oxide coating. The initial electron temperature was varied up to a factor of 5 by using 7 different pump fluences. The technique allows to derive electron and magnetization dynamics from the same raw data. This led to an electron thermalization time of 280 fs, in agreement with Ref. 1, but no delay between electron excitation and loss of magnetization was observed within the experimental time resolution. Once an electron temperature was established, the recovery of magnetization followed the classical magnetization curve[4] which appears to be valid even when electrons and lattice are not in equilibrium.

Scholl *et al.*[3] performed two-color spin-polarized time-resolved two-photon photoemission (2PPE) on 6 Å and 12 Å Ni films on Ag(100) in UHV at one fixed pump fluence. Two film thicknesses were used to change the Curie temperature from 360 to 480 K. Two different demagnetization processes were observed, a fast one in less than 300 fs, which the authors attributed to excitation of Stoner pairs, and a slow one around 500 ps which was ascribed to the excitation of spin waves. It leads to a complete demagnetization of the 6 Å film with the low Curie temperature. The decrease of magnetization for times up to 1 ns is, however, difficult to understand in view of the fact that the thermal diffusion length increases with the square root of time. This should cool the irradiated spot within the investigated time interval and partially restore the magnetization.

In view of these conflicting results for Ni it seems important to perform further experiments on electron and spin dynamics in ferromagnetic films. Our method of choice is pump-probe SHG because of its surface sensitivity and because the nonlinear magneto-optical Kerr effect is large.[5–7] First, we report on breakdown and restoration of magnetization in thin Ni and Co films on Cu(001) in UHV. For Ni films we restricted ourselves to the range of in-plane magnetization $\leqslant 8$ ML.[8,9] Second, we compare the magnetization recovery of a 7 monolayer (ML) Ni film in UHV with that of a polycrystalline bulk Ni surface in air for times up to 500 ps. Third, we show how fast magnetization breakdown proceeds on a bulk Ni surface in air. All results support the view of Ref. 2 that spin dynamics following optical excitation is a collective process determined by electron temperature T_e only, which proceeds according to the magnetization curve $M(T_e)$.[4]

We also want to mention the work of Ganping Ju *et al.*[10] where time-resolved MOKE was applied to study the spin dynamics in a ferromagnetic $CoPt_3$ alloy film after excitation with circular polarized pump pulses which create an additional nonequilibrium spin polarization. This is outside the scope of our paper where we discuss time-resolved measurements on Ni after excitation with linear polarized pump pulses which results in an equal excitation of majority and minority electrons.

The experimental setup for measurements with thin films will be described in detail elsewhere.[11] It consisted of a UHV chamber with a base pressure of about 2×10^{-10} mbar for growing thin films on a Cu(001) surface by thermal evaporation at a rate of about 0.2 ML/min. The film thickness was controlled by medium energy electron diffraction (MEED) which shows an intensity modulation with monolayer periodicity for Ni and Co films up to thicknesses of more than 10 ML, indicating layer-by-layer growth. Further annealing was done to improve the film quality.[12] The films were magnetized to saturation in the film plane perpendicular to the plane of incidence (transversal geometry) by a pair of Helmholtz coils inside the UHV chamber.

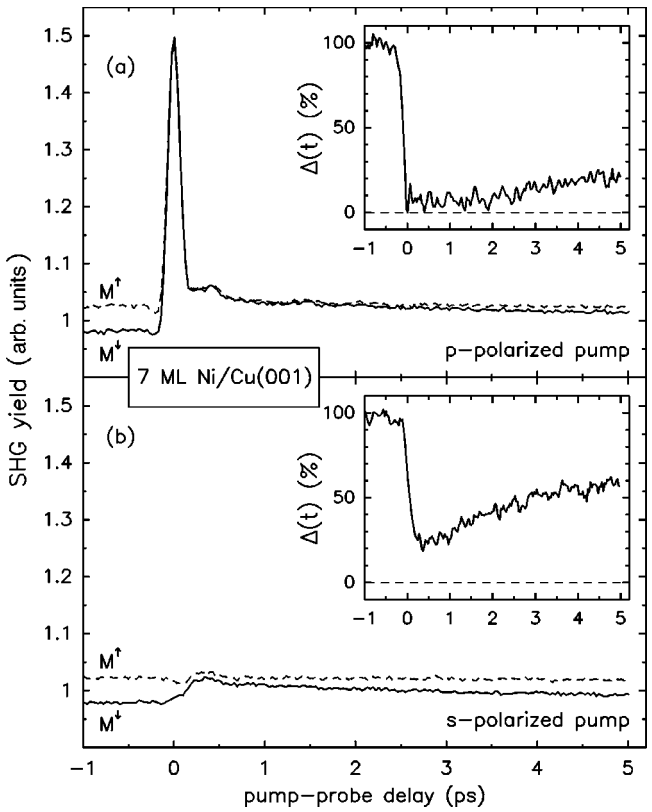

FIG. 1. Total p-P SHG yield (p-polarized fundamental and SHG) for opposite magnetization directions in transversal geometry as a function of delay between pump and probe pulses for a 7 ML Ni film on Cu(001) at 323 K. (a) and (b) show the results for p- and s-polarized pump light, respectively. The insets show breakdown and recovery of magnetization with the relative difference $\Delta(t)$ defined in the text. The applied pump fluence was 12 mJ/cm^2.

Laser pulses of 4 μJ and 150 fs/800 nm generated by a Coherent Mira 900/Rega 9000 system were split in pump and probe pulses with an intensity ratio of 4:1 and applied through a UHV window onto the film at an angle of 45°. The angle between pump and probe beams was about 3°. Both were focussed by the same lens ($f=30$ cm) into a spot of about 180 μm diameter. This resulted in a maximum pump fluence of about 12 mJ/cm^2. The polarization of the pump pulses could be changed from p to s polarization by a half-wave plate. Incident probe pulses were always p polarized and the reflected probe SHG was detected in P polarization and separated from the fundamental by a combination of a fused silica prism and a color filter. The repetition rate of the laser system was 40 kHz, sufficient to use efficient lock-in detection at about 850 Hz but low enough to prevent cumulative heating of the sample.

To obtain a better signal-to-noise ratio the experiments were done in two steps. First the probe beam was chopped and the SHG yield of the probe beam was measured at a fixed negative delay between pump and probe beams for opposite magnetization directions. Then the pump beam was chopped and the pump-induced changes of the probe SHG yield were recorded as a function of pump-probe delay time. At each delay the magnetization direction was switched by 180°. Plotted in Figs. 1 and 2 is the total SHG yield defined as the pump-induced changes at each delay point plus the yield at the negative delay.

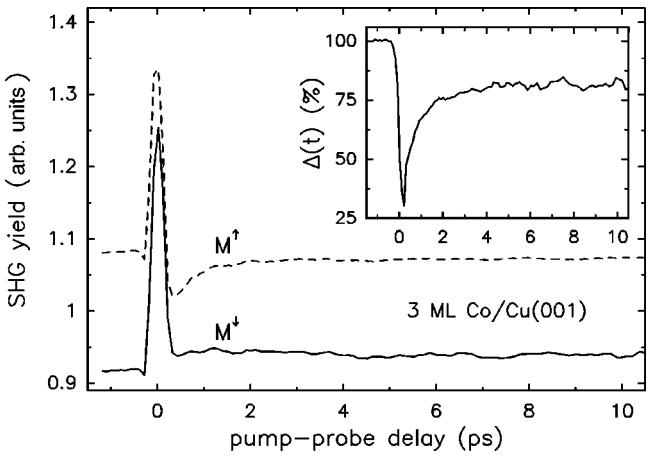

FIG. 2. Total p-P SHG yield for opposite magnetization directions in transversal geometry as a function of delay between pump and probe pulses for a 3 ML Co film on Cu(001) at 323 K. The inset shows breakdown and recovery of magnetization for an applied p-polarized pump fluence of 12 mJ/cm^2.

The difference of SHG yield for opposite magnetization directions is a measure of magnetization M. It is caused by interference of even χ^{even} and odd χ^{odd} contributions of the nonlinear susceptibility. This can be seen by forming the sum and difference of the SHG signals for opposite magnetization directions[2]

$$I^{\uparrow}+I^{\downarrow}=2I^2(\omega)[|A\chi^{\text{even}}|^2+|B\chi^{\text{odd}}|^2], \tag{1}$$

$$I^{\uparrow}-I^{\downarrow}=4I^2(\omega)|A\chi^{\text{even}}B\chi^{\text{odd}}|\cos\phi. \tag{2}$$

Here, $I(\omega)$ is the intensity of the fundamental light, A and B are effective Fresnel factors, and ϕ is an effective phase between the even and odd contributions. The assumption is that in first order the even contribution is independent of M ($\chi^{\text{even}}=\chi_0^{\text{even}}$) while the odd part depends linearly on M ($\chi^{\text{odd}}=\gamma M$) and changes sign when the direction of M is reversed. In most cases the odd contribution is small compared to the even one, and $I^{\uparrow}+I^{\downarrow}$ is dominated by the even contribution. The experimental results show that the variation of the sum with delay does not exceed a few percent which is due to the insensitivity of the optical constants on the electronic excitation for our thin film systems at 800 nm. This enables us to identify $[I^{\uparrow}(t)-I^{\downarrow}(t)]$ directly with the time dependence of the magnetization which we in turn will correlate with the electron temperature. The temperature dependence of $[I^{\uparrow}-I^{\downarrow}]$ was previously shown to follow the magnetization curve $M(T)$ for bulk nickel.[2] For thin films magnetization curves were also measured with SHG as a function of substrate temperature in thermal equilibrium between electrons and lattice[11] whereby the Curie temperatures obtained by other techniques[8,13] were reproduced.

In practice, we will deduce $M(t)$ from the relative difference $\Delta(t)=[I^{\uparrow}(t)-I^{\downarrow}(t)]/[I_0^{\uparrow}-I_0^{\downarrow}]$, where $I_0^{\uparrow}-I_0^{\downarrow}$ is the signal difference at negative delays.

Figure 1 shows the time dependence of SHG yield for a 7 ML Ni film for p- and s-polarized pump light. The difference between the SHG signals for opposite magnetization directions at negative delays is about 5%. For p-polarized pump

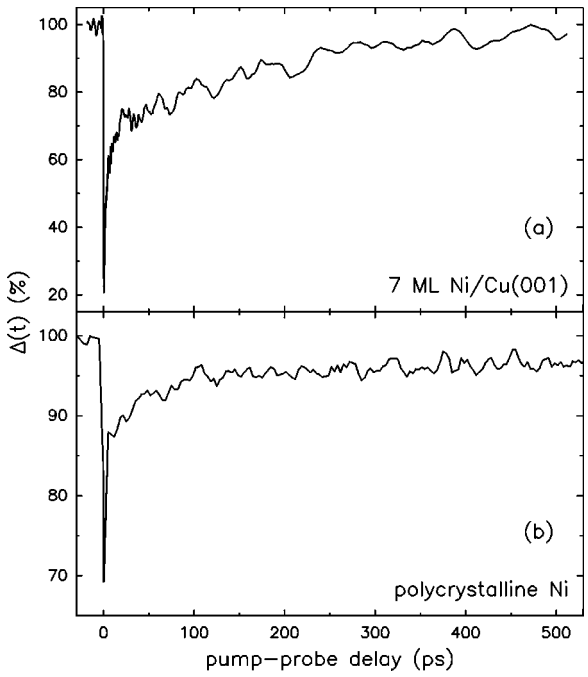

FIG. 3. Recovery of magnetization on a long time scale for (a) 7 ML Ni film on Cu(001) in UHV at 323 K (*s*-polarized pump at about 12 mJ/cm^2) and (b) bulk Ni surface in air at room temperature (*p*-polarized pump at about 6 mJ/cm^2).

light a strong correlation peak was observed at short delay times [Fig. 1(a)] which is absent for cross-polarized beams [Fig. 1(b)]. The correlation peak is caused by an induced grating[14] between pump and probe beam and is present only around zero delay within the width of the cross-correlation function. The maximum of the correlation peak was used to define zero delay. Regardless of the correlation peak the averaged signal $[I^{\uparrow}(t)+I^{\downarrow}(t)]/2$ changes by less than 6% which justifies the assertion that $\Delta(t)$ monitors the magnetization.

The breakdown of magnetization is shown in the insets of Fig. 1. For *p*-polarized pump light $\Delta(t)$ reaches saturation close to zero in a time limited only by our time resolution. Hence, the magnetization of a 7 ML Ni film can be erased completely with *p*-polarized pump pulses of 12 mJ/cm^2 for up to 2 ps. The fact that $\Delta(t)$ saturates in the first picoseconds and does not change sign proves that the time dependence of Δ is not caused by a change of the phase ϕ. After about 2 ps a slow recovery starts, indicating the onset of cooling due to thermal diffusion. For *s*-polarized pump light the absorption at 45° angle of incidence is only half as large as for *p*-polarized light, resulting in weaker heating and therefore incomplete breakdown of magnetization [cf. inset of Fig. 1(b)]. Similar measurements were done for other film thicknesses in the range of in-plane magnetization, all resulting in a magnetization breakdown faster than the pulse width and recovery times compatible with thermal diffusion in the substrate.

If the magnetization is governed by electron temperature during the first picoseconds, as we propose, any change in Curie temperature T_C should influence the loss of magnetization. This suggests a comparison of the effects in Ni and Co films. For a 7 ML Ni film $T_C \approx 400$ K, increasing only weakly with film thickness.[13] Compared to Ni, Co films have

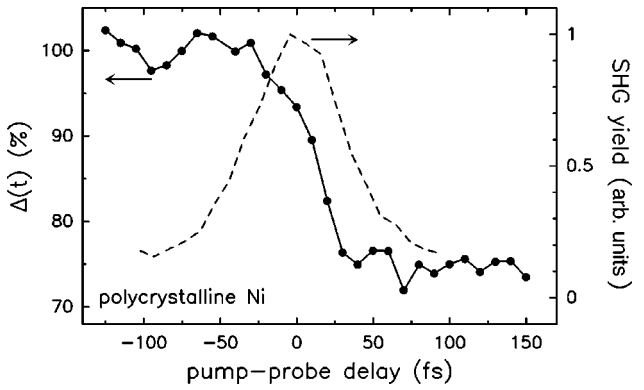

FIG. 4. Ultrafast magnetization breakdown at the surface of bulk Ni in air (solid curve) measured with 65 fs pulses at room temperature. The dashed curve represents the cross-correlation between pump and probe pulses indicating that the breakdown is limited by the pulse width.

a much higher T_C, reaching room temperature at about 1.7 ML (Ref. 15) and 600 K at 3 ML (Ref. 16). Therefore, we expect a considerably smaller reduction of magnetization for a 3 ML Co Film on Cu(001) compared to the 7 ML Ni film for the same absorbed fluence. Figure 2 shows the result. The difference between the SHG signals for opposite magnetization directions at negative delays is about 15%, three times larger than for the Ni film. This factor corresponds well to the ratio of the magnetic moments of Co and Ni which is $1.71\mu_B/0.6\mu_B$.[17] As expected, the magnetization cannot be erased completely with the same pump fluence as for the Ni film. Both breakdown and recovery times are comparable to the Ni films indicating a similar electron and spin dynamics in Ni and Co.

To examine the proposition of Scholl *et al.*[3] that phonon-magnon scattering should be responsible for a further decrease of magnetization on a time scale of some hundred picoseconds we also measured the recovery of magnetization for large delay times. Figure 3(a) shows the relative difference $\Delta(t)$ for a 7 ML Ni film as a function of pump-probe delay up to 500 ps. The data indicate a smooth restoration of magnetization with time, as expected from the temperature decrease by thermal diffusion into the substrate. To demonstrate that magnetization recovery in this time range is a common feature, we compared the thin film result with data for a polycrystalline bulk Ni surface in air, which are displayed in Fig. 3(b). The experimental setup for measurements on polycrystalline bulk Ni surfaces in air was described in Ref. 2. Apart from the fact that the degree of magnetization reduction differs for the thin film and the bulk surface due to the difference in the Curie temperature, both measurements show the same general trend. Hence, we find no indication for a loss of magnetization in this time range as reported in Ref. 3 which confirms that the magnetization of Ni is governed by electron temperature at all times. In addition, the comparison in Fig. 3 proves the compatibility of SHG measurements in UHV and in air.

The other question is whether there is any delay between electron excitation and spin relaxation. To investigate this the laser pulses ought to be as short as possible, but in view of the present discussion even an upper limit is of value. Therefore, 65 fs/800 nm pulses provided by a laser system at

the Max-Born-Institute in Berlin-Adlershof were employed. We applied a fluence at the surface spot which was comparable to that in Ref. 2. The low repetition rate of 1 kHz of the laser caused us to utilize Boxcar detection for the SHG. The result for the surface of polycrystalline bulk Ni in air is shown in Fig. 4. It can be seen that also for pulses as short as about 65 fs magnetization breakdown is completed within about 50 fs, which sets an upper limit that is determined by the laser pulse width. It is evident from this measurement that significantly shorter pulses must be used to pursue this question.

In summary, we have employed time resolved pump-probe SHG to investigate the magnetization dynamics following optical excitation in Ni and Co films on Cu(001) as well as on a bulk Ni surface. Starting point were conflicting reports in the literature about a difference between electron and spin temperature in the picosecond range and loss of magnetization by phonon-magnon scattering on a time scale of 500 ps. In our experiments we cannot reproduce these allegations. There is neither an indication for a separate spin temperature in Ni and Co nor evidence for further reduction of spin polarization after several hundred picoseconds in Ni. The observed magnetization breakdown is faster than 50 fs and the long time recovery is fully consistent with cooling by thermal diffusion. Hence we conclude that the magnetization dynamics is entirely governed by electron temperature, as suggested in Ref. 2. What happens before the electron temperature is established must be subject to further investigations with better time resolution.

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