Ultrafast metamagnetic phase transition in an elemental antiferromagnet

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We present evidence for an ultrafast optically induced antiferromagnetic-to-ferromagnetic phase transition of Mn in Co/Mn multilayers. We observe the transient ferromagnetic signal at the arrival of the pump pulse at the Mn L3 resonance using x-ray magnetic circular dichroism in reflectivity. The timescale of the effect is comparable to the duration of the excitation and occurs before magnetization in Co is quenched. Theoretical calculations point to the imbalanced population of Mn unoccupied states caused by the Co interface for the emergence of this metamagnetic phase transition.

Controlling magnetic order at high speeds requires the ultrafast manipulation of the spin degree of freedom, a central goal of spintronics [1]. Progress in lasers rendered ultrashort optical pulses as the most promising route towards the ultrafast control of magnetization [2]. The importance for technological applications and the scientific interest for the physical processes underlying ultrafast demagnetization focused a lot of research on ultrafast optical quenching of magnetic order in itinerant ferromagnetic (FM) materials after a non-adiabatic excitation at timescales comparable or even shorter than the exchange interaction [3–14].

On the contrary, reports on itinerant antiferromagnets are scarce because the absence of a macroscopic magnetic moment makes these systems difficult to study. Lately, Thielemann-Kühn et al. [15] showed that manipulation of antiferromagnetic (AFM) order is considerably faster than FM, a pivotal finding given the modern perspective for the cooperative utilization of FM and AFM components in future (opto-) spintronics [16, 17]. In this context, materials that can switch between AFM and FM order on ultrafast timescales could offer unprecedented opportunities. This phase transition, called metamagnetic, has been observed in the time domain for the first time on FeRh [18, 19] on sub-ps timescale after excitation with fs laser pulses. Later, Radu et al. [20] reported on the formation of a transient FM state at the ps timescale during the magnetization reversal of the ferrimagnetic material GdFeCo.

A critical question is how fast can we manipulate such a phase transition? In FeRh and GdFeCo, the transient FM state emerges after heating the electronic system with the concomitant modification of the exchange field that couples the spins antiferromagnetically. Afterwards, the FM state emerges either because of a Rh-mediated strong FM exchange interaction of Fe atoms in FeRh [18] or as a manifestation of the different remagnetization times between Fe and Gd sublattices in GdFeCo [20]. The lowest temporal limit for thermally activated processes, common in itinerant systems, is set by the timescale of the exchange interaction (≤100 fs) [21]. This restriction prohibits us to benefit from lasers with much shorter pulse length that are now readily available. Therefore, as the laser light sets the ultimate timescale, optical manipulation is the only means for the coherent control of magnetic order at ultimate timescales especially in metallic systems [22, 23].

A theoretical suggestion has recently been put forward for the all-optical manipulation of magnetic order on sub-exchange timescales [24]. The mechanism, named optically-induced intersite spin transfer (OISTR), is of pure optical origin as spin-selective transfer is taking place between neighboring atoms driven by the oscillating electric field of light. The process is universal, i.e., it does not depend on the material, and allows control of magnetic order only with the structure of the excitation pulse. Most recently, the observation of OISTR has been reported using time-resolved magnetic circular dichroism with extreme ultraviolet photons in FM Ni/Pt multilayers [25, 26], opening the way for the magnetic control on attosecond timescales, an order of magnitude faster than the exchange interaction. Shortly afterwards, other studies suggested the existence of OISTR at the Co/Cu(001) interface [13] and in CoPt [27] and FeNi [28] alloys using fs laser pulses indicated that traceable effects are also present in the femtosecond regime. Nevertheless, the most intriguing prediction [24] of OISTR is yet to be observed: a transient FM state in an AFM material, i.e., an ultrafast optically-driven metamagnetic phase transition.

In this Letter, we report the observation of such a transient metamagnetic phase transition in the AFM Mn in a Co/Mn multilayer, after an ultrashort laser excitation. Our sample consists of repetitions of 3 monolayers (MLs) of Mn and 3 MLs of Co, in which, under static conditions, the magnetizations of the FM Co layers are FM-aligned and the net Mn magnetization is close to zero. The latter is not expected for an odd-layers AFM film with atomically sharp interfaces to a FM material and could be explained by frustration at monoatomic steps.

at the interfaces. We unambiguously observe a transient FM state in the AFM Mn by magnetic circular dichroism in time-resolved resonant magnetic x-ray reflection (RMRXR), which is estimated to last as long as the pump pulse duration. Our experimental observations are in agreement with ab-initio calculations and identify the OISTR effect as the underlying mechanism for the emergence of this transient FM state due to the imbalanced transient population of unoccupied minority states in Mn layers caused by the contribution from the AFM-coupled interfacial Co.

Our sample was grown in an ultra-high vacuum chamber with a base pressure of 1×10^{-9} mbar, on a Cu(001) substrate held at room temperature using e-beam evaporation from a Co rod (99.998% purity) and Mn flakes (99.99% purity) in a Ta crucible. We deposited six repetitions of 3 MLs of Co and Mn and on top 14 MLs of Co as a capping layer to prevent the oxidation of the underlying multilayers by residual gas molecules in the ultra-high vacuum. During deposition, the thickness was determined by the intensity oscillations of diffraction spots in medium-energy electron diffraction while the sample cleanliness was verified by Auger electron spectroscopy. After growth, the sample was stored in a vacuum suitcase with a base pressure better than 2×10^{-10} mbar until its in-vacuum transfer to the magnetic characterization chamber.

We characterized the sample at the FemtoSpeX slicing facility [29] at the synchrotron radiation source BESSY II of the Helmholtz-Zentrum Berlin. Static and dynamic RMRXR measurements have been conducted using a magnetic field of 0.2 T with alternating direction between parallel and anti-parallel orientation relative to the x-ray propagation direction and with a fixed x-ray light helicity (see Fig. 1(a)). The time-resolved RMRXR measurements have been performed by exciting the sample with linearly-polarized 60-fs laser pulses of 800 nm wavelength and incident fluence F = 12 mJ/cm², nearly parallel to the x-ray incidence. The magnetic signal was probed with x-ray pulses of 100 fs duration, reaching the sample with a 6 kHz repetition rate, while the pump laser was operated at 3 kHz in order to detect in succession reflected x-rays from the sample with and without laser excitation. The dynamic magnetic signals have been obtained from the difference of the reflected signal with and without laser excitation at the L₃ edge of Co and Mn. The total time resolution of our experiment was 120 fs and during all measurements the sample was kept at room temperature. Because of the low intensity of the fs x-ray pulses, our experimental error was determined...
Magnetic contrast

-14
-10
-6
-2
0
0
2
6
10
Mn
0.0
0.5
1.0
1.5
Time delay (ps)
(b)
(a)
Magnetic contrast (%)

FIG. 2. Time-resolved XMCD signal from the L$_3$ edge of (a) Mn and (b) Co. Shaded blue, red regions correspond to the statistical error for the measurements based on Poisson statistics. The zero time delay is defined here at the maximum of the laser pump pulse. The red oscillating and the dashed lines represent the pump pulses and their full width at half maximum, respectively, while the light-red shaded area indicates the experimental time resolution.

by photon-counting statistics. Additional characterization of the static magnetic and structural properties of our sample have been performed at the VEKMag endstation at BESSY II after the dynamic measurements at FemtoSpeX and can be found in the supplementary section [30].

Finally, we employed \textit{ab-initio} time-dependent density functional theory (TD-DFT) calculations to identify the processes underlying our experimental observations. We performed TD-DFT calculations for 2 ML Mn on top of 3 ML Co with an impinging pump pulse with 20 fs full width at half maximum (FWHM) and 19 mJ/cm$^2$ of incident laser pump fluence, as the only input parameters of the calculation. Our model calculations are based on a fully non-collinear version of the Elk code [31, 32], where electron dynamics after laser excitation is treated by taking into account relativistic effects. Our theoretical approach considers spin and charge currents including superdiffusive currents [33, 34], spin-orbit induced flips, electron-electron scattering and charge- and spin-density waves with unit vectors larger than the size of a unit cell. During these simulations nuclei were kept fixed, however, calculation of transient Hellmann-Feynman forces indicate that the Born-Oppenheimer approximation is good these early times.

A schematic representation of our sample can be seen in Fig. 1(c). The dominant layered character of our Co/Mn multilayers has been confirmed by analysis of x-ray resonant reflectometry oscillations measured at specular geometry. Our sample has a periodicity according to the nominal deposition profile with slight interfacial diffusion [30]. We have calculated the intensity of the pump pulse’s electric field as a function of the distance from the sample’s surface [30] (see Fig. 1(c)). Our calculations show that 60.1% of the incoming infrared light is reflected while $\approx 26.6\%$ is absorbed by the Co layers (13.9% is the share of the cap layer) and 13.3% by the Mn layers, respectively. We estimate that 0.23 and 0.26 photons are absorbed per pulse per Mn and Co atom in our sample, respectively.

Figure 2 displays the time-resolved magnetic signal measured at the L$_3$ resonances of Mn and Co. In static conditions, Co layers do not experience AFM interlayer coupling while the applied magnetic field (0.2 T) is enough to achieve full magnetic saturation. After the excitation pulse, in Fig. 2(b), we see a strong demagnetization of Co. Fitting the demagnetization curve to an exponential decay function [30] results in a demagnetization time constant of 155 $\pm$ 29 fs, in agreement with studies on Co/Pt [35] and Co/Pd [36] multilayers.

Most importantly, in Fig 2(a) we observe virtually no magnetic contrast on Mn at negative time delays in accordance with the AFM nature of Mn thin films. Statistically, the sample shows a small magnetic dichroism ($\approx 1.8\%$) antiparallel to the Co magnetization [30], which is below the experimental error in the time-resolved RMXR measurement of Mn. While one would expect a higher uncompensated magnetic moment in atomically smooth 3-ML Mn layers, imperfections and atomic-scale roughness at the Co/Mn interfaces will lead to magnetic frustration and can explain the nearly vanishing static Mn net magnetization. At the arrival of the excitation pulse, we observe an onset of the magnetic signal of Mn that peaks at 8.2%. Right after the pump pulse, the Mn signal returns to its initial ground state value. The maximum lifetime of the transient FM state in Mn is equal or lower than the time resolution of our experiment.

We attribute the observed transient FM order in Mn to the OISTR effect. We surmise that the FM order in Mn lives roughly as long as the pump pulse is present ($\approx 60$ fs), given the reported observations of the same effect in Ni/Pt [25] and theoretical considerations [24]. The estimated lifetime of the metamagnetic phase transition is consistent with the timescale needed for this excited state to lose coherence due to spin-orbit coupling in an itinerant magnet [22]. We have to stress that the Co magnetic moment sets the preferential orientation of the interatomic magnetic current [22]. We have to stress that the Co magnetic moment sets the preferential orientation of the interatomic magnetic current [22].
The transient FM phase in Mn emerges at a point when Co has not yet considerably demagnetized [37], suggesting the optical nature of the metamagnetic phase transition. Another mechanism that might play a role in our experiment is superdiffusive transport [34]. However, given that the transient FM alignment of Mn layers occurs synchronously with the pump pulse arrival and that, in the meantime, the magnetic signal reduction in Co is small, superdiffusive transport likely does not play a significant role at this early time period.

Our first-principles calculations can qualitatively explain our experimental observations. We choose to compare our sample with a system with 2 ML Mn on top of 3 ML Co to minimize the total starting magnetization from Mn layers. The simulation of a layered system with zero Mn magnetization as the one studied experimentally would require a large supercell, making the *ab-initio* approach unfeasible. The main conclusions from the calculations do not change, since the parity of Mn layers does not play a role in the emergence of the FM state, as OISTR is mainly an effect between nearest neighbors and decays fast with distance [24]. Finally, the laser excitation was selected shorter for convenience, as the timescale of the AFM-to-FM transition depends only on the FWHM of the excitation pulse [24]. As shown in Ref. 24, longer and weaker pulses result in the same physics but with higher computational cost. Therefore, our current approach and conclusions are also valid on the timescale of our experimental excitation.

Our calculations clearly show the transition from AFM to FM alignment of the Mn layers after the arrival of the pump pulse (see Fig. 3a, b). The onset of the FM state starts right before our pump pulse reaches its half maximum and peaks simultaneously with its vector potential, while Co shows a slower demagnetization in agreement with our experimental observations (see Fig. 2). The underlying mechanism for the transient FM phase is revealed in Fig. 3 (c)-(h), where the unoccupied minority spin density of states acts as a sink for excited majority spin electrons from the neighboring Mn layer.
The spin swapping between Mn neighbors, facilitated by their AFM coupling, as well as the higher unoccupied state filling of the atoms at the interface (Mn1) from the AFM-coupled reservoir of Co majority electrons drive the transient metamagnetic phase transition in Mn.

In summary, we presented compelling evidence of a transient FM phase of AFM Mn in Co/Mn multilayers due to the OISTR effect. The transition is driven by the electric field of the pump pulse in a fs timescale, much faster than the FM-order quenching in Co, while the induced macroscopic magnetic moment of Mn aligns with the adjacent ferromagnet. Our calculations show that the transient FM state originates from the imbalance of intersite transfer of electrons in Mn atoms due to the asymmetry introduced by the Co interface. The lifetime of the phase transition is comparable to the pump-pulse duration in agreement with the theoretical predictions. Our observation validates the hallmark prediction of an important mechanism for ultrafast optical manipulation of magnetic order and showcases a transient metamagnetic phase in a monoelemental antiferromagnet that can play an important role in ultrafast optospintronic devices.

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