Femtosecond Laser Excitation Drives Ferromagnetic Gadolinium out of Magnetic Equilibrium

Robert Carley,1,2 Kristian Dobrich,1 Björn Frietsch,1,2 Cornelius Gahl,2 Martin Teichmann,1,2 Olaf Schwarzkopf,3 Philippe Wernet,3 and Martin Weinelt2,∗

1Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin, Germany
2Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
3Helmholtz Zentrum für Materialien und Energie (BESSY II), Albert-Einstein-Straße 15, 12489 Berlin, Germany

(Received 10 April 2012; published 31 July 2012)

The temporal evolution of the exchange-split Δf-like Σ valence bands of the 4f-fermagnet gadolinium after femtosecond laser excitation has been studied using angle-resolved photoelectron spectroscopy based on high-order harmonic generation. The ultrafast drop of the exchange splitting reflects the magnetic response seen in femtosecond magnetic dichroism experiments. However, while the minority valence band reacts immediately, the response of the majority counterpart is delayed by 1 picosecond and is only half as fast. These findings demonstrate that laser excitation drives the valence band structure out of magnetic equilibrium.

DOI: 10.1103/PhysRevLett.109.057401 PACS numbers: 78.20.Ls, 71.45.Gm, 73.20.At, 78.47.–p

Since its first experimental observation [1,2] optical excitation of electronic spins and ultrafast magnetization dynamics have seen intense research [3,4]. Nevertheless, details of the microscopic processes involved remain controversial and a variety of models are being explored to explain the optically-induced sub-ps (de)magnetization. These include Elliott-Yafet scattering [5], electron-electron spin-flip and exchange scattering [6–8], and superballistic electron transport [9]. Likewise the role of the spin-orbit interaction has been discussed [10–12]. Experimental signatures of magnetic dynamics have been explored in detail, elucidating the role of the laser-induced hot electron distribution and state blocking in magneto-optics and x-ray magnetic circular dichroism (XMCD) [13]. The importance of the exchange interaction has been highlighted by recent work on alloys [14], including demonstrations of deterministic ultrafast optical magnetic switching [4,15]. However, only one photoemission study has addressed changes in the exchange-split bulk band structure of ferromagnets following optical demagnetization [16].

Typically, the spin system is assumed to have a defined temperature that can be extracted from the (de)magnetization at all times following optical excitation. This assumption has been repeatedly questioned [17,18] but until now not directly addressed experimentally although new magnetic phases have been observed in magnetic systems driven far from equilibrium by laser excitation [15,19]. Given that it takes ≈ 2 ps to reach thermal equilibrium between the electronic system and the lattice after optical pumping, the question remains how the ultrafast and equilibrium magnetization processes compare.

The nature of its magnetic ordering (Fig. 1) makes gadolinium an ideal system in which to unravel equilibrium vs. nonequilibrium charge and spin dynamics. The half-filled 4f shell leads to a large localized magnetic moment (7μB) per atom. This is exchange-coupled to the itinerant (5d6s)3 valence electrons and polarizes their spins. These then align the moments of adjacent atoms in an indirect exchange interaction explained by the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory, leading to magnetic ordering and exchange splitting (ΔEex) of the valence bands. The thermal magnetic phase transition has already been studied by spin- and angle-resolved photoelectron spectroscopy (ARPES) [20,21]. Time-resolved studies have established that a weak spin-lattice interaction decouples the 4f spins from the lattice [22], giving a slow response time of 40 ps [23–25]. This provides a fast spin excitation channel in the valence band decoupled from slow 4f spin-lattice effects.

In this Letter we perform time-resolved ARPES with femtosecond extreme-ultraviolet (XUV) pulses from high-order harmonic generation to map the transient valence band structure of Gd(0001) after excitation by an intense femtosecond infrared (IR) pulse. We observe that the minority components of the valence band [26] probes the sample magnetization but reflects the sample magnetization but

The XUV radiation was generated by focusing 775 nm, 45 fs, 1 mJ IR pulses into 100 mbar argon. The p-polarized 35.6 eV, 100 fs pulses with a minimum bandwidth of 150 meV were delivered to the sample via a toroidal grating monochromator. Tuning the XUV photon energy to ≈ 36 eV probes the third Brillouin zone in the Γ-M direction, revealing the minority and majority components of the Δf-like Σ valence band (Fig. 1). In the ferromagnetic phase at 100 K the valence...
band is exchange split, whereas above the Curie temperature of 293 K, $\Delta E_{\text{ex}}$ vanishes [20].

In the time-resolved experiments, we record ARPES images as a function of the IR pump–XUV probe delay for an absorbed pump fluence of $1.2 \text{ mJ cm}^{-2}$. Pump pulses were stretched to 300 fs to minimize space-charge distortion of the spectra. At each pump-probe delay PE spectra were obtained as shown in Fig. 2. A space-charge shift induced by the IR laser was corrected by reference to the $4f$ peaks positions, which we have found by ARPES measurements with HeII radiation not to change between the ferro- and paramagnetic phases. The resulting binding energies are shown in Fig. 3(a). The surface state position and dynamics agree with published values [27]. At late times, when the system is in equilibrium [24], the valence band positions agree with high-resolution PE data [28].

The most striking feature of Fig. 3(a) is that within the first 2 ps the majority and minority components of the valence band exhibit different dynamical responses to the laser excitation. Specifically, the minority band reacts earlier than the majority band by $\approx 1$ ps, and the rate of change of the minority binding energy is also twice as fast as its majority counterpart. To our knowledge, these distinct dynamics of the two sub-bands have not been predicted by contemporary theory, so such a large difference in reaction times was not expected. At $\approx 1$ ps the minority binding energy starts to decrease again, and by $\approx 2.5$ ps both bands attain constant binding energies until $\approx 20$ ps. Between about 30 and 60 ps we see small changes attributed to $4f$ spin-lattice coupling, after which the binding energies correspond to those measured in thermal equilibrium [28].

Since in thermal equilibrium $\Delta E_{\text{ex}}$ is reduced with decreasing sample magnetization, it was calculated from the fitted positions of the minority and majority bands to facilitate comparison with other studies and is shown in Fig. 3(b). The initial reduction in $\Delta E_{\text{ex}}$ was fitted with a single exponential with a time constant of $0.86 \pm 0.15$ ps, in agreement with recent XMCD and magneto-optical Kerr effect (MOKE) studies [25,29]. It follows the fall in the electronic temperature [Fig. 3(b), inset axis], implying spin-flip scattering and/or transport of hot, photoexcited carriers plays a role in the demagnetization at early times. Between approximately 4 and 50 ps, $\Delta E_{\text{ex}}$ remains constant within the experimental error. In this time window, the demagnetization rate due to spin-flip scattering has fallen with the electronic temperature. After 50 ps $\Delta E_{\text{ex}}$ recovers as the system cools.

The agreement between our $\Delta E_{\text{ex}}$ data and magnetization dynamics from MOKE and XMCD show our experiment to be a complimentary tool in this field. Furthermore, our consideration of only a small region of $k$ space is justified because we see identical dynamics throughout the probed range of $k_{||}$. Since $\Delta E_{\text{ex}}$ is determined to first order by the $4f$
spin moment and the 4f-valence band exchange integral [30], it lies between 0.6 and 0.9 eV everywhere in the Brillouin zone [31,32]. We therefore expect to see similar dynamics for this band at all points in the Brillouin zone.

To rule out a thermal origin for the changes in the band structure at very short times, we plot in Fig. 4 the binding energy of the minority and majority bands against $E_{\text{ex}}$. The hysteresis-like loops in Fig. 4 show that the valence band structure exhibits different behavior during laser-driven demagnetization [lower branches of the majority (blue, up triangles) and minority (red, down triangles) loops] from that during thermal remagnetization (upper branches). We note that at exactly zero pump-probe delay, a single majority data point moves to higher binding energy by $60 \text{ meV}$. This shift may be related to the recently observed coherent magnetic response [19] and requires investigation with better time resolution.

It is known from spin-resolved photoemission studies of gadolinium [20] that demagnetizing the sample by heating is accompanied by simultaneous reduction of both $E_{\text{ex}}$ (Stoner behavior) and the spin polarization of the exchange-split bands (spin mixing). We therefore assume the changing binding energies of the bands in our data indicate a loss of spin polarization due to spin mixing. Spin mixing in the minority band is synchronous with the electronic excitation. In contrast, the majority band remains at constant binding energy and therefore does not appear to undergo spin mixing until $1\text{ ps}$ later.

It might seem useful to invoke electron scattering to explain our observations. Indeed, several studies point to different spin-flip scattering rates for minority and majority electrons [8,33,34]. Scattering arguments, however, neglect the coupling between the valence and 4f core electrons, which is artificial since they are linked by the RKKY interaction. Therefore to understand the dynamics, we consider here the coupling between the valence and 4f spins shown in Fig. 1. Laser excitation with linearly polarized light cannot flip the spin of an electron and the 1.5 eV pump energy does not directly excite electrons in the observed bands. However spin-flip processes (exchange, electron-phonon, etc.) do occur in the valence band as hot electrons scatter. When the spin of a majority valence electron is inverted, this can be transferred to the 4f electron spin by the exchange interaction, leaving the majority valence band spin unchanged. This is equivalent to emitting a magnon and reduces the magnetization by $2\mu_B$. The analogous spin-flip in the minority valence band, which is also exchange-coupled (albeit probably with different strength than the majority), cannot be transferred to...
the 4f electrons because they are already nearly saturated with majority character [33]. The 4f electrons thus act as a large majority spin reservoir, allowing the position of the majority valence band to remain unchanged for some time. At our starting temperature of 100 K the probability of launching a magnon will be far higher than for absorbing one [7], so we expect negligible magnon absorption at early times. Magnon absorption can explain the shift of the Leibniz Gemeinschaft via Pakt für Forschung und Grosser, and R. Peslin. This work received funding from dynamical changes of the exchange-split band structure equilibrium. More generally, these results suggest that these dynamics to its majority counterpart on the sub-ps time scale. Therefore there is no unique spin temperature on this time scale and the system is out of magnetic order on this time scale and the system is out of magnetic order and majority spin components of the valence band in ferromagnetic gadolinium. Interpretation from the perspective of spin mixing suggests that these differences arise through the majority spin saturation of the 4f electrons, which favours spin-flip energy transfer from the exchange coupling, the minority valence band exhibits different dynamics to its majority counterpart on the sub-ps time scale. Therefore there is no unique spin temperature on this time scale and the system is out of magnetic equilibrium. More generally, these results suggest that dynamical changes of the exchange-split band structure can considerably increase spin-flip scattering probabilities in laser-driven ultrafast demagnetization.

We thank M. Wietstruk, F. Noack, N. Zhavoronkov, R. Grosser, and R. Peslin. This work received funding from the Leibniz Gemeinschaft via Pakt für Forschung und Innovation, LASERLAB-EUROPE, and the Deutsche Forschungsgemeinschaft.

*weinelt@physik.fu-berlin.de