Ultrafast dynamics of 4f electron spins in TbFeCo film driven by inter-atomic 3d–5d–4f exchange coupling

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Abstract

The ultrafast demagnetization dynamics of 3d and 4f spins, respectively, in FeCo and Tb of TbFeCo alloy film are studied independently by employing a dual-color time-resolved magneto-optical Kerr spectroscopy. The demagnetization dynamics of 3d and 4f spins are independently probed, respectively, by 800 and 400 nm light. Two-step demagnetization dynamics are observed for both the 3d and 4f spins under the excitation of 800 nm laser. In particular, the onset of 4f spin dynamics presents a delayed time with respect to the one of 3d spin dynamics. Those results clearly reveal a strong inter-atomic 3d–5d–4f exchange coupling which drives the first-step subpicosecond ultrafast demagnetization process of 4f spins, and a spin(4f)-lattice coupling which drives the second-step slower demagnetization process of 4f spins. A numerical calculation based on four temperature model reproduces the coupling characteristics in the demagnetization dynamics, and reveals the energy evolution dynamics among the different subsystems. These results provide a direct demonstration of strong coupling dynamics between the two spin subsystems in rare earth-transition metal alloy occurring within subpicosecond timescale, and show a new approach for ultrafast control of 4f spins via an indirect excitation.

Introduction

Ultrafast spin dynamics in magnetic system has been an important and active field due to its scientific significance and great potential for developing new magnetic and spintronic technologies [1–20]. Many researches concentrated on the rare earth (RE) metals [20–25], in which the magnetism mainly comes from the localized 4f electrons. The 4f electrons are generally deeply buried below the Fermi level \((E_F)\) [20], and hence difficult to be directly excited by ultrashort laser pulse. It was believed that the demagnetization dynamics of 4f electrons is caused by the intra-atomic 5d–4f coupling [20] or the spin(4f)-lattice coupling [21, 22]. RE metals are regarded as an excellent model for studying spin–spin or spin–lattice coupling.

Time-resolved x-ray magnetic circular dichroism (TR-XMCD) experiments on RE metals [21, 22] usually exhibited two-step demagnetization dynamics, including a subpicosecond ultrafast demagnetization process and a slower one with a timescale of ten-to-hundred picoseconds. The mechanisms of 4f demagnetization were also intensively discussed [20–22]. However, recent TR photoemission experiments [23–25] revealed the subpicosecond ultrafast process induced by near-infrared (NIR) femtosecond (fs) laser was from the response of itinerant 5d electrons instead of 4f magnetization [22, 24, 25], while only the slower demagnetization dynamics was related to the spin(4f)-lattice coupling [22, 25]. It seemed to suggest that in RE metals the intra-atomic 5d–4f spin–spin coupling cannot directly drive the demagnetization of 4f spins.
On the other hand, ultrafast spin dynamics in rare earth–transition metal (RE-TM) ferrimagnetic alloys has also attracted much more attentions due to the significant potential applications of RE-TM alloys [2–16], particularly in ultrafast magnetic recording [2–12]. By means of TR-XMCD, Radu et al. have demonstrated the ultrafast magnetization reversal dynamics of the RE and TM components in a GdFeCo film under an excitation of 800 nm fs laser [2]. Then, what is the mechanism of the ultrafast 4f demagnetization in Gd component which should be one of the bases of ultrafast magnetization reversal of Gd? Spin-lattice coupling can be excluded because of the much longer timescale [22, 25], while spin–spin coupling can be a probable path. Nevertheless, for RE-TM materials, it is still not clear how the 4f demagnetization dynamics is coupled to other spin subsystems or what the mechanism of ultrafast demagnetization of RE component is.

Recently, indirect evidence about the coupling between RE-4f and TM-3d demagnetization dynamics was reported. Mekonnen et al. observed an anomalous two-step demagnetization dynamics of the TM component in GdCo and GdCoFe alloy films, and performed a calculation based on a four-temperature (4T) model, indirectly revealing the role of inter-atomic 3d–5d–4f exchange coupling on the demagnetization dynamics [26]. For further verification and clearer insight of the 3d–5d–4f coupling dynamics, direct observations of the 4f spin dynamics are very necessary. Tb-based RE-TM alloy is just a good experimental system, because 4f spins of Tb are buried shallowly around 2.4 eV below \( E_F \) and can be accessible by visible light instead of x-ray [27]. Khorsand et al. found the dynamics of the 4f and 3d spins in TbFeCo alloy could be studied selectively by choosing the wavelength of light below and above 610 nm respectively [27]. However, they could not observe the coupling dynamics between the 3d and 4f spins because 400 nm pumping light was used to simultaneously excite 3d and 4f electrons, led to the 3d–4f coupling dynamics submerged by directly excited 4f spin dynamics. Moreover, pump–probe magneto-optical Kerr (MOKE) experiments with two wavelengths were also used on RE-TM alloys in different cases [28–30], but the 3d–4f coupling dynamics still has not been demonstrated directly.

In this work, we study the fs-laser-induced ultrafast demagnetization dynamics in a TbFeCo alloy film by using a dual-color TR-MOKE measurement. The dynamics of 3d and 4f spins are independently observed, respectively by 800 and 400 nm probe light. We find the 4f spin dynamics presents a delayed subpicosecond ultrafast process followed by a slower process under the excitation of 800 nm laser. The emergence of the subpicosecond ultrafast process provides direct evidence for the inter-atomic 3d–5d–4f coupling. The coupling dynamic characteristics are also reproduced by a 4T model calculation and discussed in details.

**Experiment**

TR-MOKE technique is used in the measurement of ultrafast magnetization dynamics. Linearly polarized laser pulse train at a central wavelength of 800 nm, with a duration of \( \sim 100 \) fs and a repetition rate of 1 kHz, is generated from a Ti:sapphire regenerative amplifier. The laser beam is split into pump and probe with a fluence ratio of pump to probe larger than 30. The central wavelength of the pump or probe light is optionally converted to 400 nm by second harmonic generation (SHG) using a 1 mm thick BBO crystal. The numerical simulation considering group delay dispersion (not shown) demonstrates that the duration broadening of SHG pulses can be negligible. Both the pump and probe beams are incident normally on the sample surface. The pump one is focused to a spot of \( \sim 150 \) \( \mu \)m in diameter, while the probe spot is located at the center of the pump spot and is approximately one half smaller than the pump spot to avoid heat gradient within the probed area. We use an optical balanced bridge to detect the polar Kerr rotation of the reflected probe light. The signals are then measured by a lock-in amplifier synchronized to an optical chopper. All measurements are performed at room temperature.

The samples studied is an amorphous TbFeCo ferrimagnetic alloy film with thickness of 102 nm prepared by magnetron sputtering. Unequal FeCo- and Tb-atom moments at room temperature are antiferromagnetically coupled to each other via a strong 3d–5d–4f exchange interaction [15, 27]. The magnetization compensation temperature and the Curie temperature of the sample are determined as \( \sim 380 \) K and \( \sim 508 \) K, respectively.

The magnetic moment of FeCo is carried by the itinerant 3d electrons near the \( E_F \). The 3d spins can be easily excited and probed by the light at 800 nm wavelength [1, 5, 12]. For Tb, the majority of magnetic moment (about 97%) is carried by the localized 4f electrons [27, 31], while the 5d conduction electrons only carries \( \sim 3\% \) of total magnetic moments. Since the 4f shell of Tb atoms is buried around 2.4 eV below \( E_F \), the 4f spins cannot be accessed directly by the light at 800 nm wavelength corresponding to a photon energy of \( \sim 1.55 \) eV. However, one can get access to it using the light at 400 nm. The element sensitivity of Kerr response in TbFeCo has been demonstrated in visible and NIR range in [27]. In particular, it was shown that the Kerr signal probed at 800 nm came from 3d moment of FeCo, i.e. the contribution of Tb is negligible in the NIR range, while the Kerr rotation probed at 400 nm mainly arose from 4f moment of Tb (accounts for \( \sim 90\% \)). Therefore, in our experiment probe light at 800 and 400 nm wavelengths is employed to monitor the dynamics of the 3d and 4f spins,
respectively. In addition, the pump light is also switched between 800 and 400 nm to optionally excite the 4f spins.

**Experimental results and discussions**

The out-of-plane Kerr hysteresis loops are first measured under a variable magnetic field applied perpendicularly to the film plane using probe light respectively at 800 and 400 nm wavelengths, and plotted in figure 1. One can see that the Kerr rotation of the two loops under the same saturated field of ±8 kOe are of opposite sign, revealing antiferromagnetic coupling between FeCo and Tb moments in TbFeCo, and also demonstrating the independent probing ability on both 3d and 4f spin subsystems, respectively by 800 and 400 nm light. The Kerr loop measured at 800 nm presents rectangle-like shape indicating a coercivity of 5.14 kOe and revealing the strong out-of-plane magnetic anisotropy of the film. However, the Kerr loop probed at 400 nm slants gradually with the increase of applied field, which agrees well with the viewpoint that the direction of RE moments is randomly canted from the direction anti-parallel to the TM moments in heavy RE-TM alloys [32].

Next, we carry out TR measurements on the demagnetization dynamics respectively using probe light at two wavelengths of 800 and 400 nm under the excitation of 800 nm pump light pulses with a fluence of 12.5 mJ cm$^{-2}$. As mentioned above, the 800 nm pump pulse can only excite the 3d electrons of FeCo and the 5d electrons of Tb. The demagnetization dynamics are measured in remanence state to avoid the emergence of external-field-driven magnetization precession [17, 33] or magnetization reversal across the ferrimagnetic compensation point [3, 12]. For RE-TM system, it is demonstrated that the remanence state was stable after excited by controllable amount of pump pulses without helicity [11], and the magnetization dynamics measured in remanence state can represents the temperature-induced change in magnetization [4, 12]. In other words, the TR Kerr signals measured here are dominated by the change of magnetization magnitude caused by laser excitation.

The demagnetization dynamics of 3d and 4f spins obtained for an identical initial magnetization state are plotted in figure 2 by solid line and dashed line, respectively. Their original Kerr signals are out of phase (inverted up and down) due to antiferromagnetic coupling between FeCo and Tb moments. Here the 4f spin dynamics is plotted upside down for convenient comparison. The 3d spin dynamics probed at 800 nm presents a two-step demagnetization followed by a slow magnetization recovery. Such two-step demagnetization dynamics, which includes a strong ultrafast component and a weak slower one within tens of picoseconds, is different from the typical one-step demagnetization dynamics of 3d spins in pure TMs like Fe and Co [1, 20]. Similar two-step demagnetization dynamics of FeCo(Co) component were also reported in GdFeCo(GdCo) alloy films [26], where the second-step slower demagnetization process occurring within hundreds of picoseconds accounted for a large proportion in total demagnetization amplitude, and was attributed to lattice-spin(3d) coupling. However, here the amplitude of the first-step ultrafast demagnetization process seems absolutely dominant, and the timescale of the second-step demagnetization process is much shorter than the corresponding one in GdFeCo or GdCo.
As blue dashed line shows in figure 2, the dynamics of 4f spins probed at 400 nm wavelength also presents a two-step demagnetization including a significant ultrafast process and a weak slower one within dozens of picoseconds. Similar two-step demagnetization was also demonstrated by TR-XMCD spectroscopy on pure RE metals [21, 22]. However, it is worth noting that the first-step ultrafast demagnetization process has different origin in previous TR-XMCD and here our experiment. The ultrafast demagnetization process observed by TR-XMCD on pure RE metals was believed to originate from ultrafast spin-flip scattering of 5d spins [22, 24, 25], whereas here it arises from demagnetization of 4f spins. In other words, in pure RE metals the 4f spin subsystem lacks an ultrafast spin–spin direct coupling channel, but only has a slower spin–lattice coupling channel which causes the second-step slower demagnetization process. Consequently, it was shown that 5d–4f spin coupling in pure RE metals cannot directly drive the demagnetization of 4f spins. While here in RE-TM alloys the second-step slower demagnetization process can be similarly attributed to spin–lattice coupling. However, what is the origin or driving force of the first-step ultrafast demagnetization of 4f spins? The only possible origin is the coupling between 3d–5d and 4f spin subsystems. In particular, it should be reminded that 3d spins are from TM FeCo, while 5d–4f spins from RE Tb. Therefore, a strong inter–atomic spin coupling dynamics is directly observed in TbFeCo alloy for the first time by 400 nm light probe. This result means that in RE-TM alloys the 3d–5d–4f spin coupling is strong enough to directly drive the ultrafast 4f demagnetization, which is contrasted with the ineffectiveness of 5d–4f spin coupling in pure RE metals. It can be understood that 5d spins only carry the minority of total moment of RE atom, while the rest majority is carried by 4f spins, so that the tiny 5d spin subsystem is insufficient to directly drive a huge 4f spin subsystem in pure RE metals [22, 24]. However, 3d spins carry entire atomic moment comparable to that of 4f spins hence the 3d–5d spin subsystem is able to directly drive the 4f spin subsystem in RE-TM alloys when 3d spins are excited.

To get a deeper insight into the demagnetization processes of the 3d and 4f spins, the demagnetization dynamics are measured with a higher temporal sampling rate, as plotted in figure 3(a). The transient reflectivity which was believed to reflect the transient electron temperature [1] is also measured at 800 and 400 nm wavelength respectively by using single photodetector instead of optical balanced bridge. It can also serve as a reference of the zero time-delay alignment. The transient reflectivity probed at 800 nm wavelength is plotted in figures 2 and 3(a) by dashed–dotted lines. The inset (a1) shows a zoom-in of three dynamic processes within the first 5 ps. One can see that the electron temperature rises up to the maximum by ~0.31 ps. Both the demagnetization dynamics of 3d and 4f spins are obvious two-step processes. The ultrafast first-step demagnetization process ends at about 0.6 and 1.85 ps respectively for the 3d and 4f spins, indicating that the response of 3d spins is faster than the one of 4f spins, but slower than the one of electrons.

Furthermore, it is also worth noting in the inset (a1) that the onset of 4f demagnetization is delayed by ~0.5 ps, not concurrent with the 3d demagnetization. However, such a delay did not appear in the 4f demagnetization dynamics of TbFeCo pumped by 400 nm light pulses [27], revealing that the ultrafast 4f demagnetization dynamics excited by 800 nm pump pulses is driven indirectly by energy transfer rather than directly by photon excitation. On the other hand, the first-step ultrafast demagnetization of 3d spins ends at
∼0.6 ps. This ending point overlaps quite well with the ∼0.5 ps delayed onset of the 4f demagnetization. It also supports that the 4f demagnetization is driven by 3d spins via 3d–5d–4f exchange coupling between the FeCo and Tb spin subsystems. In addition, a small dip at the beginning of the second-step 3d demagnetization (see the inset (a2) of figure 3) seems also to provide the evidence about the energy and angular momentum transfer between the two spin subsystems, as mentioned in [26].

One may note the weak rising tail before the delayed fast-rising edge in 400 nm probed Kerr signal. It should originate from the weak Kerr effect of 3d spins. Although Kerr rotation probed at 400 nm is dominated by 4f moment of Tb (∼90%), it still contains weak contribution from 3d moment of FeCo (∼10%) [27]. The 3d demagnetization dynamics occurs earlier than the 4f demagnetization process, and hence a weak tail appears before the delayed 4f dynamics takes place. The tail signal is in phase with the Kerr signal of 4f demagnetization. That is because for 3d metals the Kerr rotation probed by 400 nm light is out-of-phase with the one by 800 nm light [34]. As a result, here Kerr signals from 3d and 4f spins are in phase as 400 nm probe light was used.

As further comparison, we measure the 3d demagnetization dynamics (by 800 nm probe light) under the excitation of 400 nm pump pulses, as plotted in figure 3(b). In this case, only an ultrafast demagnetization process occurs, and ends at ∼0.76 ps followed by a magnetization recovery. Such one-step subpicosecond demagnetization dynamics is typical for 3d metals, such as Fe and Co [1, 20]. It further proves that the second-step slower demagnetization process and also the small dip observed in the dynamics excited by 800 nm pulses are related to the 3d–5d–4f coupling. Under the 400 nm excitation, the 4f spins can be directly excited by photons. As a result, the energy transfer between the two spin subsystems would be inapparent, and the coupling phenomena would be concealed, leading to the demagnetization dynamics of 3d and 4f spins seem like that they are excited separately [27].

To deeply understand the demagnetization dynamics of 3d and 4f spins, quantitative analysis of the dynamics is very necessary. As mentioned before, the demagnetization dynamics under the 800 nm excitation present two-step processes, and thus can be approximated by a biexponential sum decay function. The measured demagnetization dynamics can be described by the convolution of the biexponential sum decay function with the autocorrelation of the pump and probe pulses (approximately Gaussian) [2, 35], which is written as

Figure 3. (a) Laser-induced demagnetization and transient reflectivity dynamics measured with a higher temporal sampling rate (other configurations are the same to those of figure 2). The red and blue solid lines represent the best fittings of the demagnetization dynamics. The inset (a1) and (a2) show zoom-in pictures of the dynamics. Both the 3d and 4f demagnetizations obviously present two-step processes. A delayed response is observed on the 4f spins because it is driven indirectly by inter-atomic spin coupling rather than directly by photon excitation. (b) Demagnetization dynamics measured by 800 nm probe light under an excitation of 400 nm light pulses.
Numerical calculation and analysis

In order to further understand the demagnetization dynamics observed in our experiments, we make a dynamic simulation based on a 4T model which was proposed by Mekonnen et al [26]. For the case of TbFeCo, the 3d spins of FeCo and the 4f spins (and also the minority 5d spins) of Tb are treated as two different spin reservoirs. They interchange energy with each other, and also with electron and lattice (phonon) reservoirs, respectively. The 4T model can be written as followings [26]:

\[
\begin{align*}
\frac{dM}{dt} &= -A_1 M(t) F(t) - A_2 M(t) G(t),
\end{align*}
\]

where

\[
F(t) = \frac{1}{\tau_1} \left[ 1 - \exp \left( -\frac{t}{\tau_1} \right) \right] + \frac{1}{\tau_2} \left[ 1 - \exp \left( -\frac{t}{\tau_2} \right) \right] + A_0, \quad t \geq t_0,
\]

and

\[
G(t) = -B \exp \left( -\frac{t^2}{w^2} \right),
\]

Here \( B \) is the area-normalized factor of the Gaussian autocorrelation function, \( w \) is the full width at half maximum (FWHM) of the Gaussian pulses, \( \tau_1 \) and \( \tau_2 \) are the time constants of the two demagnetization processes, while \( A_1 \) and \( A_2 \) are the amplitudes of the two demagnetization processes. \( A_0 \) is the background (baseline). Taking account for the delayed onset of the demagnetization of 4f spins, a delay time \( t_0 \) is introduced.

Equation (1) is used to best fit the data of demagnetization dynamics in figures 3(a) and (b), as shown by the solid lines. All parameters are determined by the fittings and listed in table 1. Particularly for the 3d demagnetization dynamics excited by 400 nm pulses, single exponential decay function is used to fit the one-step demagnetization process. One can see that the two processes of the 4f demagnetization are obviously slower than corresponding those of the 3d one under identical excitation of 800 nm pulses. The time constant of the first-step ultrafast demagnetization of 800 nm excited 3d demagnetization, \( \tau_1 \approx 0.25 \) ps, is close to the one (0.28 ps) of 400 nm excited 3d demagnetization, and also to the corresponding one (~0.2 ps) reported in [27] (measured under an 400 nm excitation). However, for 4f demagnetization, \( \tau_1 = 0.61 \) ps, is larger than the corresponding one (~0.4 ps) reported in [27]. The latter shows the difference between the 4f demagnetization dynamics driven by inter-atomic coupling and by direct excitation. The delayed \( t_0 = 0.46 \) ps onset of the ultrafast 4f demagnetization further shows the origin of 3f spin dynamics via inter-atomic exchange coupling. It is concerned that the demagnetization times for the excitation at 400 and 800 nm may not be directly comparable due to the probable difference in absorption. But we note the 400 nm excited 3d spin dynamics measured under a larger pump fluence (not shown) still presents a one-step demagnetization with time constant of 0.27 ps, implying that the demagnetization time in TbFeCo films is not strongly dependent on excitation energy, and thus supporting the rationality of above discussion.

It is more interesting to note that the demagnetization proportion of 3d spin subsystem, \( A_1 + A_2 = 0.63 \), is almost equal to the one of 4f spin subsystem, \( A_1 + A_2 = 0.61 \), which is both very reasonable and also the evidence of strong antiferromagnetic RE-TM coupling in TbFeCo. The ratio of the ultrafast demagnetization amplitude to total demagnetization for 3d spins is, \( A_1/(A_1 + A_2) = 82.5\% \), while this ratio for 4f spins is, 57.4\%, which suggests the spin transfer coefficient via ultrafast 3d–5d–4f exchange coupling channel is only 57.4%/82.5% = 69.6\%. Such a lower spin transfer coefficient can explain why ultrafast demagnetization process via 5d–4f coupling is difficult to observe in pure RE metals such as Gd and Tb because the contribution of 5d–4f coupling to demagnetization amplitude of 4f spins is at most ~2%.
Here subscripts $e$, $s$, and $l$ denote the electrons, spins and lattice subsystems, respectively. The superscripts FeCo and Tb are used to distinguish the two different spin subsystems. $T$ and $C$ are the phenomenological temperature and the specific heat of each subsystem, respectively, while $G$ is the coupling coefficient between every two subsystems. In particular, $G_{ss}$ is the spin–spin coupling coefficient between FeCo and Tb, which is dependent on the 3d–5d–4f exchange coupling. $P(t)$ is the heat perturbation pulse from laser excitation acting on the electron subsystem and is approximately Gaussian form. Equation (4) is solved numerically using the Runge–Kutta method. In the calculation, $C_e = 3.0 \times 10^8$ J (m$^3$ K$^{-1}$) is taken as a constant based on the Debye law [36], while $C_v(T_e) = \gamma T_e$, where $\gamma = 2.0 \times 10^3$ J (m$^3$ K$^{-1}$) [1,37]. For $P(t)$, a 100 fs FWHM and a peak power density of $4.2 \times 10^{21}$ W m$^{-3}$ are used. Here we consider the 800 nm excitation case, in which the 4f electrons cannot directly absorb the photons. The initial temperature is set to be 300 K. Other parameters are tuned within reasonable ranges until the calculation results qualitatively agree well with the experimental ones.

Figure 4(a) shows the calculation results of 4T model. They reproduce the main characteristics of the experimental dynamics in Figure 3(a). To discuss conveniently, we divide the time window into three regions $\Delta t_1$, $\Delta t_2$, and $\Delta t_3$, for convenient discussions. (b) Calculation results by setting $G_{ss}$ to zero while all other parameters are kept as the values used in (a).
coupling. One can see that there is a subpicosecond delay before the significant increase of \( T_s^{Tb} \), which just agrees with the \( \sim 0.5 \) ps delayed onset of the 4f demagnetization shown in figure 3.

In \( \Delta t_2 \) region, the energy flows continuously from FeCo spins to Tb spins, leading to a slight drop of \( T_s^{FeCo} \). Note that in the second equation of 4T model, the contribution of \( -G_0^{FeCo}(T_s^{FeCo} - T_s) \) term can be neglected after \( T_s^{FeCo} \) and \( T_s \) reach quasiequilibrium, hence the rest two terms would dominate the evolution of \( T_s^{FeCo} \). The drop of \( T_s^{FeCo} \) means that the energy flow from FeCo spins to Tb spins is even larger than that from electron reservoir to FeCo spins at this time. Such slight drop (dip) is observed as well, as shown in the inset (a2) of figure 3. On the other hand, \( T_s^{Tb} \) keeps a fast increase until it is close to \( T_s^{FeCo} \).

In \( \Delta t_3 \) region, \( T_s \) reaches its maximum and exceeds \( T_s^{FeCo} \). Thus, the energy reversely flows to FeCo spins from lattice subsystem, leading to a slow increase of \( T_s^{FeCo} \), that is the second-step process of 3d demagnetization. On the other hand, \( T_s^{Tb} \) and \( T_s^{FeCo} \) gradually reach a quasiequilibrium state, and together approach to \( T_s \) which has been in equilibrium with \( T_s \). This agrees with the above viewpoint that both the second-step processes of 3d and 4f demagnetization can be attributed to the spin-lattice coupling [22, 26]. Note that \( T_s^{Tb} \) is lower than \( T_s^{FeCo} \) when \( T_s^{Tb} \) starts its second-step slow rising process. That explains why the second-step process of 4f demagnetization accounts for a larger ratio in total demagnetization amplitude than that of the 3d one.

The 4T-model-based calculation shown in figure 4(a) reveals the energy evolution dynamics among four different subsystems, and explains the origins of characteristics appearing in the demagnetization dynamics. In the calculation, the spin specific heats are taken as \( C_s^{FeCo} = 0.36 \times 10^{16} \) J (m\(^{-3}\) K\(^{-1}\)) and \( C_s^{Tb} = 0.92 \times 10^{17} \) J (m\(^{-3}\) K\(^{-1}\)). The coupling coefficients are taken as \( G_0^{FeCo} = 5.60 \times 10^{17} \) W (m\(^{-3}\) K\(^{-1}\)), \( G_0^{FeCo} = 1.82 \times 10^{16} \) W (m\(^{-3}\) K\(^{-1}\)), \( G_0^{Gd} = 0.55 \times 10^{16} \) W (m\(^{-3}\) K\(^{-1}\)), \( G_0^{Gd} = 0.80 \times 10^{15} \) W (m\(^{-3}\) K\(^{-1}\)), \( G_0^{Tb} = 0.29 \times 10^{16} \) W (m\(^{-3}\) K\(^{-1}\)), and \( G_0 = 3.65 \times 10^{16} \) W (m\(^{-3}\) K\(^{-1}\)), respectively. The parameters of FeCo are close to the typical values of metals [1]. \( G_0^{Tb} \) is much weaker than \( C_0^{FeCo} \), which is reasonable because of the ineffective excitation of the 800 nm laser pulse on the 4f electrons and spins. Being different from the case of GdFeCo [26] in which \( G_0^{Gd} \) is much weaker than \( G_0^{FeCo} \), here \( G_0^{Tb} \) has the same order of magnitude as \( G_0^{FeCo} \) due to the stronger spin–orbit coupling of Tb which results in the stronger spin-lattice coupling [21, 27].

The most notable parameter, \( G_{so} \), is much larger than corresponding value estimated in GdFeCo [26], meaning a much stronger inter-atomic spin–spin energy transfer. There are two possible origins. One is different potential energy of 4f shell of Gd and Tb atoms. The 4f shell of Gd are deeply buried \( \sim 8.4 \) eV below \( E_F \), while this value for Tb is only \( \sim 2.4 \) eV. As a result, the 3d–5d–4f energy transfer for TbFeCo should be easier than for GdFeCo due to the smaller potential energy difference between the 4f electrons and the 3d–5d electrons in the conduction band. The other may be different orbital moment of Gd and Tb atoms. The net orbital moment of Gd is zero due to its half-filled 4f shell. Thus, the spin–orbit interaction in Gd is very weak [20]. However, a non-spherical 4f distribution of Tb results in a non-zero orbital moment and thus a strong spin–orbit interaction [21, 27]. That may add an extra inter-atomic energy transfer way from the 3d spins of TM to the 4f spins via the coupling between the orbital moments of 3d and 4f electrons.

For further verifying the validity of above discussion on the calculation results, we try to cut off the coupling between 3d and 4f spins in the calculation by setting \( G_{so} \) to zero while all other parameters are kept as the values used in figure 4(a), the results are shown in figure 4(b). In this case, the first-step fast rising of \( T_s^{Tb} \) cannot be reproduced, but only a slow increase process still occurs. Additionally, the two-step feature and the dip of \( T_s^{FeCo} \) disappear too. All these further prove that the inter-atomic spin–spin coupling is just the origin of the first-step fast demagnetization of 4f spins (\( T_s^{FeCo} \)), and also related to the two-step demagnetization and the dip occurred in the 3d spin (\( T_s^{FeCo} \)).

**Conclusion**

In conclusion, the ultrafast demagnetization dynamics in TbFeCo alloy film are studied by employing a dual-color TR-MOKE measurement. Both the 3d and 4f spin dynamics present two-step demagnetizations under the 800 nm laser excitation, but the 3d spin dynamics presents one-step demagnetization under the 400 nm excitation. Particularly, a delayed ultrafast 4f demagnetization process is observed under the 800 nm excitation. The first-step ultrafast demagnetization dynamics of 4f spins is driven by the inter-atomic 3d–5d–4f coupling between 3d and 4f spins, while the second-step slower demagnetization dynamics is done by the spin(4f)-lattice coupling. The 4T-model-based calculation reproduces the coupling characteristics in the demagnetization dynamics, and reveals the energy evolution dynamics among the different subsystems. These results provide a direct demonstration of strong coupling dynamics between the two spin subsystems in RE-TM alloy occurring within subpicosecond timescale, and show a new approach for ultrafast control of 4f spins via an indirect excitation.
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