Hot-Electron-Driven Enhancement of Spin-Lattice Coupling in Gd and Tb 4f Ferromagnets Observed by Femtosecond X-Ray Magnetic Circular Dichroism

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Femtosecond x-ray magnetic circular dichroism was used to study the time-dependent magnetic moment of 4f electrons in the ferromagnets Gd and Tb, which are known for their different spin-lattice coupling. We observe a two-step demagnetization with an ultrafast demagnetization time of 750 fs identical for both systems and slower times which differ sizeably with 40 ps for Gd and 8 ps for Tb. We conclude that spin-lattice coupling in the electronically excited state is enhanced up to 50 times compared to equilibrium.

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Laser-induced magnetization dynamics has high potential for ultrafast data-storage applications [1] and a microscopic understanding of the underlying processes is essential for device optimization and tuning. In this context switching the magnetic order by intense, ultrashort laser pulses explores the speed limit of magnetic recording. Next to its technological relevance magnetization dynamics driven by femtosecond (fs) laser pulses challenges our microscopic understanding of magnetism: (i) Bigot *et al.* [2] and Zhang *et al.* [3] suggest that the light field is involved in magnetization dynamics. (ii) Battiato *et al.* propose superdiffusive spin transport as a mechanism of ultrafast demagnetization [4]. (iii) Koopmans and coworkers have developed an empirical model based on spin-orbit mediated electron spin-flip scattering. Their concept implies a material dependent demagnetization time and connects itinerant and rare earth ferromagnets [5]. Ultrafast laser-induced magnetization dynamics has been established for the 3d metals and a number of alloys [6–14]. In view of angular momentum conservation a change in the magnetization M requires transfer of angular momentum from M to some other reservoir. The crystal lattice is a prominent candidate here, which turns spin-lattice coupling into an essential, but barely investigated interaction in ultrafast magnetization dynamics.

In this Letter we report on laser-induced magnetization dynamics in the lanthanide ferromagnets Gd and Tb. By time-resolved x-ray magnetic circular dichroism (XMCD) at the M_5 absorption edges we probe directly the 4f magnetic moment, out of reach for magneto-optical techniques. We identify for both materials two separate demagnetization processes, a slower quasiequilibrium one and an ultrafast one active in the electronically excited state. The time constants for the slower process differ for the strong direct spin-lattice coupling in Tb (8 ps) and the weaker indirect interaction in Gd (40 ps). The ultrafast process agrees for both elements (0.74 vs 0.76 ps) and is active while hot electrons are present. It involves an enhancement of the indirect spin-lattice coupling, which leads to a pronounced increase in the momentum transfer rates from the magnetization to the lattice in Gd by as much as 50 times.

The heavy lanthanides Gd ($4f^7$) and Tb ($4f^8$) are well known for their magnetic properties as a function of occupation of the 4f orbital. While the spin quantum number S decreases as the 4f shell is more than half filled (Gd $S = 7/2$, Tb $6/2$), the orbital quantum number L increases (Gd $L = 0$, Tb 3) [15]. The magnetic moment per atom μ_{at} follows Hund's rules (Gd $7.55\mu_B$, Tb $9.34\mu_B$ [16]), where the excess from the integer value is attributed to spin polarization of the 5d6s valence electrons. Figure 1 depicts

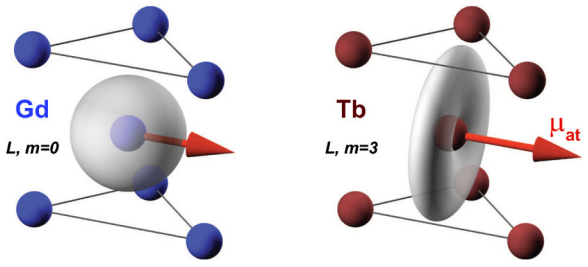

FIG. 1 (color online). Orbital wave-function distributions within an hcp unit cell for L, $m = 0$ and 3. The $m = 3$ nonspherical distribution of Tb couples to the ion cores via single ion anisotropy, which is absent for the spherical $m = 0$ state of Gd.

the L, $m = 0$ and L, $m = 3$ angular distribution of the $4f$ orbital of Gd and Tb, respectively; m is the magnetic quantum number. A pronounced coupling of the orientation of μ_{at} to the neighboring ion cores and hence to the lattice follows for Tb from the nonspherical $4f$ distribution since spin-orbit interaction couples the direction of the spin moment to the $4f$ orbital. Such a nonspherical distribution links a rocking of the atomic magnetic moment directly to a lattice vibration and vice versa. For the spherical distribution of the half filled Gd $4f$ shell this direct coupling is absent (Fig. 1). Indeed, the magnetic anisotropy constant K_2 describing the energy required to rotate M with respect to the basal plane of the hcp lattice is in Gd more than 2 orders of magnitude smaller than in Tb [15]. Also magnon excitations reflect this difference in L. Avoided crossings in the magnon dispersion of Tb explained by magnon-phonon coupling [17] are absent in Gd [18,19]. The magnetic anisotropy in Gd is, however, nonzero due to $4f$-$5d$ coupling and the spin-orbit interaction of $5d$ electrons [20]. We refer to such a valence electron mediated spin-lattice coupling as indirect.

Optical pump–x-ray probe experiments were performed at the femtosecond slicing facility of BESSY II [21]. The $5d6s$ valence electrons were excited by 1.5 eV laser pulses of 50 fs duration at a fluence of $F = 3 - 5$ mJ/cm^2 with the sample held in an applied magnetic field of 5 kOe at an equilibrium temperature of 140 K. We measured x-ray transmission for poly-crystalline $Y(50\text{ nm})/R(10\text{ nm})/Y(5\text{ nm})$ films grown on a freestanding 0.5 μm thick Al substrate; R = Gd,Tb. The x-ray photon energy was tuned to resonantly excite the $3d_{5/2}$ core-level electrons to the unoccupied $4f^1$ states with a binding energy of 4 eV above E_F [22]. Since optical transitions between $4f$ and $5d$ require photon energies far above 1.5 eV, $4f$ levels do not participate in the optical excitation [23] and therefore XMCD can be used as a reliable monitor of M [24]: pump-induced refilling of $4f$ levels and saturation effects do not affect the XMCD signal.

Figure 2(a) shows the transmission spectra for M parallel (+) and antiparallel (−) to the helicity of circularly polarized x-ray pulses without laser excitation. XMCD is determined from the difference of the absorption for opposite M. Comparing XMCD signals before and 200 ps after laser excitation [Fig. 2(b)] exhibits a pronounced pump-induced change. The sum of the spectra (not shown) remains unaffected even though the temperature is increased by the optical excitation. This guarantees that the change in XMCD is a purely magnetic effect.

We proceed to the magnetization dynamics and analyze the time-dependence of the XMCD signal. At first, we employed x-ray pulses of about 10 ps duration, which are available in the low-α operation mode of BESSY II [25]. Figure 3 depicts the time-dependent XMCD signal for Gd and Tb normalized to the value before optical excitation. For both materials we find a pronounced demagnetization,

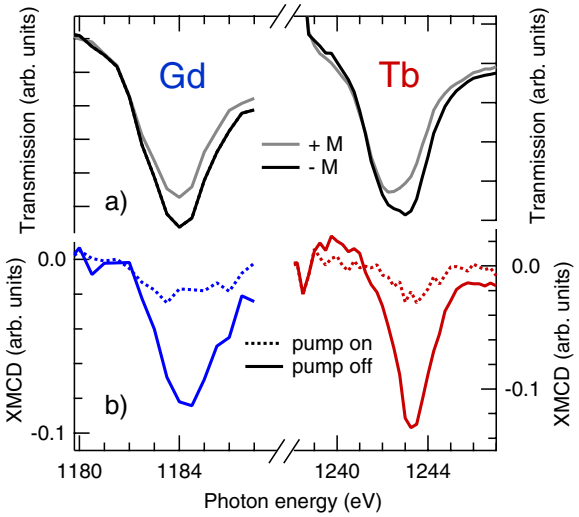

FIG. 2 (color online). (a) X-ray transmission at the M_5 absorption edges of Gd and Tb films recorded for opposite magnetization direction (black and gray lines) with 10 ps circularly polarized x-ray pulses. (b) XMCD signals of Gd and Tb before and 200 ps after laser excitation (solid and dotted lines).

but the detailed behavior is different. For Gd the minimum of M is reached after 200 ps in a two-step process. The inset indicates that about half of the final demagnetization occurs within the 10 ps pulse duration of the x-ray pulse, while the second process lowers M until 200 ps. We fit the Gd data by a biexponential decay convoluted with the x-ray pulse duration and determine a characteristic time constant of $\tau_{eq}^{Gd} = 40 \pm 10$ ps for the slower process. Electrons and phonons have equilibrated after 1 ps [26]. Therefore, we refer to delays >1 ps as a quasiequilibrium and <1 ps as an electronically excited state. The obtained τ_{eq}^{Gd} is characteristic for the weak indirect spin-lattice coupling in Gd ($L = 0$ cf. Fig. 1) in quasiequilibrium, since it is $\gg 1$ ps. Our finding substantiates previous experimental and theoretical results [27–29]. From the change in M stemming from this quasiequilibrium process at a delay of τ_{eq}^{Gd} we determine an angular momentum transfer rate of $\sigma_{eq}^{Gd} = 0.026^{+0.009}_{-0.005}\mu_B$/ps considering M at 140 K [30]. In Tb the minimum of M is reached already after 20 ps indicating a faster demagnetization, which is a consequence of the direct spin-lattice coupling ($L = 3$ cf. Fig. 1). The cooling mediated recovery of the initial magnetization is described by an exponential behavior during several 100 ps. In Gd diffusive cooling and slow demagnetization occur on similar time scales and lead to a plateau; in Tb cooling occurs after demagnetization and a recovery of M is observed at delays >20 ps.

Now three questions remain open. (i) What is the fast demagnetization time scale in Gd? (ii) Does Tb also show two distinct demagnetization time scales and if yes (iii) do both differ with respect to Gd? To answer these questions we employed fs x-ray pulses which we obtain by femtosecond slicing of the electron bunches in the storage ring

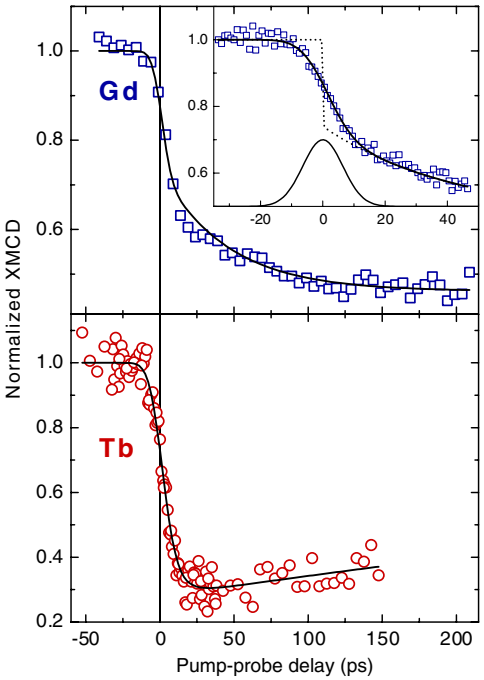

FIG. 3 (color online). Time-dependent XMCD signals for Gd (top) and Tb (bottom) measured by 10 ps x-ray probe and 50 fs laser pump pulses. Solid lines indicate fits to the data. The inset depicts Gd data in a smaller time window with the actual time-resolution of 16 ps indicated. The biexponential fit (solid line) highlights the two-step demagnetization process and the dashed line indicates the behavior expected for an instantaneous first step.

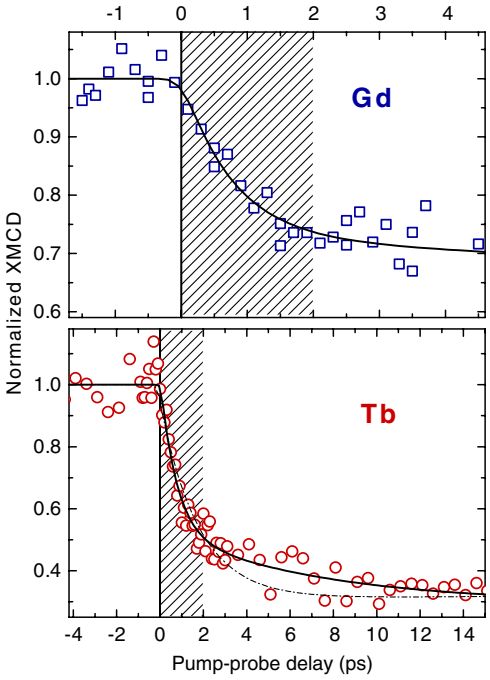

FIG. 4 (color online). Time-dependent XMCD signals for Gd (top) and Tb (bottom) measured with fs x-ray pulses. Note the different time intervals. Solid lines depict biexponential fits determined by simultaneously fitting the fs and ps time-resolved data (cf. solid lines in Fig. 3). A single exponential (dash-dotted line) for Tb yields an unsatisfactory fit.

[21,31]. Figure 4 confirms a clear reduction of M for both elements. In Gd we find after 3 ps a normalized XMCD signal of 0.7, identical to the level at which the slower demagnetization process sets in (inset in Fig. 3). Employing the fs x-ray pulses we resolve the initial, fast demagnetization process in Gd. Also for Tb we find a sizeable drop of M within 2 ps (dashed areas in Fig. 4).

To determine the characteristic time scales, the ps and fs time-resolved data have been fitted simultaneously by biexponential functions taking into account the different x-ray pulse durations (solid lines in Figs. 3 and 4). For Tb we obtain $\tau_{\mathrm{eq}}^{\mathrm{Tb}} = 8 \pm 3$ ps, which translates to an angular momentum transfer rate of $\sigma_{\mathrm{eq}}^{\mathrm{Tb}} = 0.29^{+0.17}_{-0.08}\mu_B/\mathrm{ps}$. We explain this process as being mediated by direct spin-lattice coupling under quasiequilibrium conditions persisting at corresponding delays >1 ps. This is much faster than $\sigma_{\mathrm{eq}}^{\mathrm{Gd}} = 0.026\mu_B/\mathrm{ps}$ determined for the indirect interaction in Gd, which demonstrates that the direct spin-lattice coupling stemming from the nonspherical $4f$ orbital distribution accelerates the demagnetization process in Tb.

Next, we focus on the ultrafast demagnetization process. From our fits we determine within error bars identical times $\tau_{\mathrm{ex}}^{\mathrm{Gd}} = 0.76 \pm 0.25$ ps and $\tau_{\mathrm{ex}}^{\mathrm{Tb}} = 0.74 \pm 0.25$ ps. These times are shorter than reported for Gd/Fe multilayers [13] and similar to reports on TbFe alloys [14]. Since they are clearly longer than the pulse durations we rule out coherent processes promoted in Ref. [2]. Note that our observations are likewise not compatible with demagnetization via superdiffusive spin transport [4]. The ultrafast component of the demagnetization is 50% of the total loss in M and thus too large to be explained by transport of the $5d$ electrons.

The $4f$ and $5d$ states are strongly coupled by intra-atomic exchange [32], which provides the possibility of spin transfer from the $4f$ shell to the conduction band. However, a mere transfer and accumulation in the conduction band can be excluded because (i) the transferred moment is in Tb and Gd considerably larger than the conduction-electron spin polarization and (ii) time-resolved magneto-optical Kerr effect (MOKE) experiments performed at Gd(0001), which probe primarily the conduction band spin polarization and will be presented in a forthcoming publication, demonstrate a reduction of MOKE signal concomitant with the XMCD one. Considering that the optically excited electrons in Gd equilibrate with the crystal lattice during 1 ps [26] the ultrafast demagnetization occurs as long as the system remains electronically excited. Our results demonstrate an efficient hot electron mediated momentum transfer to the lattice and determine the corresponding transfer rates of magnetic moment to the lattice to $\sigma_{\mathrm{ex}}^{\mathrm{Tb}} = 3.1^{+1.5}_{-0.8}\ \mu_B/\mathrm{ps}$ and $\sigma_{\mathrm{ex}}^{\mathrm{Gd}} = 1.5^{+0.7}_{-0.4}\ \mu_B/\mathrm{ps}$. Compared to the quasiequilibrium

processes discussed above these rates are for Tb 10 and for Gd 50 times larger. We propose that the intra-atomic $4f$-$5d$ exchange interaction, about 100 meV [32], mediates this acceleration in the electronically excited state, as by means of the $4f$-$5d$ coupling a spin-flip scattering process in the conduction band affects the $4f$ electrons as well and drives the ultrafast demagnetization via indirect spin-lattice coupling [5].

In contrast to itinerant ferromagnets, the dominant part of M in lanthanides is generated by the $4f$ electrons and is considerably larger for Gd and Tb than for Fe, Co, and Ni. Thereby, during the transfer of angular momentum from the magnetization to the lattice, several spin flips in the conduction band are required to obtain the same relative demagnetization as in a $3d$ ferromagnet. That is why in both $4f$ elements the ultrafast process lasts longer than in the $3d$ transition metals [5,21,33], although the momentum transfer rates are comparable, e.g., $\sigma_{\mathrm{ex}}^{\mathrm{Ni}} = 2.7\mu_B/\mathrm{ps}$ for Ni [21].

Finally, we compare our results with the model calculations of Ref. [5]. In agreement we find laser-induced demagnetization of lanthanides on two time scales. However, the orbital momentum of the $4f$ shell cannot be neglected because we observe $\sigma_{\mathrm{eq}}^{\mathrm{Tb}} = 11 \cdot \sigma_{\mathrm{eq}}^{\mathrm{Gd}}$. Reference [5] does not consider direct spin-lattice coupling, shown here to be essential, and predicts a figure of merit for the demagnetization time that is proportional to the ratio of Curie temperature and magnetic moment T_C/μ_{at}. Applying this to Gd ($T_C = 293$ K, $\mu_{\mathrm{at}} = 7.55\mu_B$) and Tb ($T_C = 225$ K, $\mu_{\mathrm{at}} = 9.34\mu_B$) suggests that demagnetization in Gd is faster than in Tb by a factor of 1.6. Even within our conservative error bars our results cannot support this estimation; the faster demagnetization times coincide for Tb and Gd. Furthermore these times compare well with the time scale of electron-phonon equilibration [26]. We consider therefore that the time interval during which the faster demagnetization process is active is determined by electron-phonon interaction. A similar τ_{ex} for Gd and Tb is very plausible since their conduction-electron and crystal lattice properties are widely comparable.

In conclusion magnetization dynamics of the $4f$ moments in Gd and Tb occurs on two time scales. The slower picosecond time scale is determined by the equilibrium spin-lattice coupling following the $4f$ occupation. The fast femtosecond time scale is comparable for Gd and Tb and shows a pronounced enhancement of the conduction-electron mediated indirect spin-lattice coupling. We expect this mechanism to be operative also in the $3d$ ferromagnets but hard to unravel due to the delocalized character of the magnetic moment.

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