Photo-induced antiferromagnetic-ferromagnetic and spin-state transition in a double-perovskite cobalt oxide thin film

Yujun Zhang1,2,3✉, Tsukasa Katayama4,5,6, Akira Chikamatsu6,7, Christian Schüßler-Langeheine8, Niko Pontius8, Yasuyuki Hirata3, Kou Takubo3, Kohei Yamagami3, Keisuke Ikeda3, Kohei Yamamoto3, Tetsuya Hasegawa6 & Hiroki Wadati2,3,9

Investigation of ultrafast dynamic behaviors can provide novel insights about the coupling mechanisms among multiple degrees of freedom in condensed matters, such as lattice, magnetism and electronic structure. Here we investigate both the ferromagnetic (FM) and antiferromagnetic (AFM) dynamics of a strongly correlated oxide system, GdBaCo2O5.5 thin film by time-resolved x-ray magnetic circular dichroism in reflectivity (XMCDR) and resonant magnetic x-ray diffraction (RMXD). A photo-induced AFM-FM transition characterized by an increase of the transient XMCDR (sensitive to FM order) beyond the unpumped value and a decay of RMXD (sensitive to AFM order) was observed. The photon-energy dependence of the transient XMCDR and reflectivity could be interpreted as a concomitant photo-induced spin-state transition (SST). The AFM-FM transition and SST couple with each other in the time domain, resulting in unusual dynamic behaviors of the magnetism.

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1 Institute of High Energy Physics, Chinese Academy of Sciences, Yuquan Road 19B, Shijingshan District, Beijing 100049, China. 2Graduate School of Materials Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan. 3Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8581, Japan. 4Research Institute for Electronic Science, Hokkaido University, N20W10, Kita, Sapporo 001-0020, Japan. 5JST-PRESTO, Kawaguchi, Saitama 332-0012, Japan. 6Department of Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, Japan. 7Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan. 8Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Straße 15, 12489 Berlin, Germany. 9Institute of Laser Engineering, Osaka University, Suita, Osaka 565-0871, Japan.

✉email: zhangyujun@ihep.ac.cn
Ultrafast magnetic dynamics and transient magnetic states induced by optical excitation have attracted a lot of research interest. Pioneered by the observation of the ultrafast demagnetization in Ni metal, the magnetic dynamics of various material systems are intensely investigated to characterize the relevant timescales related to the magnetic degree of freedom. With the rapid development of synchrotron x-ray sources with pulsed time structures, the role of probe in pump-probe experiments can be played not only by optical lasers but also by synchrotron x-rays or x-ray free electron lasers. Synchrotron x-ray can provide multiple probing techniques with element specificity, such as x-ray magnetic circular dichroism (XMCD), resonant magneto-optic Kerr effect (RMXD), etc. Capturing the element-specific dynamic behaviors of not only ferromagnetic (FM) order, but also antiferromagnetic (AFM) order and complex magnetic structures become possible by employing synchrotron-based resonant magnetic x-ray diffraction (RMXD), which cannot be accessed by optical laser probes.

Materials with magnetic phase transitions are interesting from both views of fundamental science and practical application. Investigation of the magnetic dynamics can provide new perspectives to understand their magnetic phase transitions. One typical example is photo-induced AFM-FM transition observed in FeRh alloy. FeRh exhibits an AFM-FM transition at ~370 K with increasing temperature and laser-pumping can promote AFM FeRh to a transient FM state. However, due to the low photon energies of the magnetic sensitive Fe and Rh, such resonances, as well as the large Q-vector of the AFM order in FeRh, it is technically unfeasible to directly investigate the dynamics of the AFM order even by using the synchrotron x-ray probes.

Recently, double perovskite REBaCo$_2$O$_{5.5}$ (5 < $x$ < 6, RE: rare earth elements) systems have been continually studied due to their intriguing physical properties such as metal-insulator transition, AFM-FM transition, spin-state transition/ordering and high oxygen ionic conductivity, etc. As schematically shown in Fig. 1(a), due to the different ionic sizes of RE and Ba ions, a site of the perovskite lattice is often ordered into alternating RE and Ba layers. The oxygen concentration in these systems is often variable, leading to high oxygen mobility through the lattice. When $x$ ≈ 5.5, the oxygen vacancies can order into columns along a-axis, resulting in non-equivalent Co sites coordinated by either oxygen octahedra or oxygen pyramids, which cannot be accessed by synchrotron-based SST at octahedral Co$^{3+}$ sites. The nominal valence state of Co is 3+ and the competition between crystal field splitting and Hund coupling results in various spin-states such as low-spin (LS, $t^6_2$ $e^0_3$, $S$=0), high-spin (HS, $t^6_2$ $e^2_3$, $S$=2) and intermediate-spin (IS, $t^6_2$ $e^1_3$, $S$=1) states. The spin-state of Co$^{3+}$ is sensitive to temperature, pressure, magnetic field, epitaxial strain, and lattice distortions, etc.

AFM-FM transitions coupled with spin-state transition (SST) was observed in some systems like GdBaCo$_2$O$_{5.5}$, i.e., Antiferromagnetism with an ordering vector of (0 0 0.5) below ~230 K was detected in GdBaCo$_2$O$_{5.5}$ by RMXD thanks to its small AFM Q-vector, providing the possibility to investigate the dynamics of both the FM and AFM orders simultaneously. A metal-insulator transition at ~350 K in GdBaCo$_2$O$_{5.5}$ (GBCO) was reported to be relevant to a SST at octahedral Co$^{3+}$ sites, which is also promising to be triggered by laser excitation instead of elevated temperature. In this work we investigate the photo-induced FM and AFM dynamics of GBCO thin film by time-resolved TR XMCD and TR-RMXD at Co L resonance within one experimental system. Photo-induced enhancement of XMCD and decay of the RMXD were clearly observed, indicating a photo-induced AFM-FM transition. Photon energy dependence of the transient XMCD and reflectivity suggests a concomitant photo-induced SST. Both the electronic state change and the competition between AFM and FM exchange interactions simultaneously contribute to the observed magnetic dynamics.

## Results and discussions

### Characterization of the static properties

The 35-nm thick epitaxial GBCO thin film ($a$=$b$=7.81Å, $c$=7.529Å, the unit cell shown in Fig. 1(a)) was grown on SrTiO$_3$(001) substrate by pulsed laser deposition and the detailed sample characterizations are reported elsewhere. Note that our GBCO film has finite magnetization in the AFM phase, which should be attributed to the competition between AFM and FM exchange interactions, either the canting of AFM moments or the coexistence of AFM and FM phases. The experimental setups of TR-XMCDR and TR-RMXD are schematically shown in Fig. 1(b) and explained in detail in the Methods part.

Figure 2 (a, b) show the static XMCD of the GBCO thin film. Reflectivity $R$ and XMCDR are defined as $R$=$(R_+ + R_-)/2$ and XMCDR=$(R_+ - R_-)/2$, respectively, where $R_+$ and $R_-$ are the reflectivity measured by applying positive/negative magnetic
fields. In the photon energy scans (Fig. 2(a)), it can be observed that Co $L_3$ resonance is located near Ba $M_5$ resonance and the XMCDR mainly appeared in the range from 775 eV to 782 eV, which represents the Co magnetization. The thickness fringes in $\theta$-2$\theta$ reflectivity curves at the Co $L_3$ resonance (Fig. 2(b)) are consistent with the nominal film thickness. An incident angle of $\theta=5^\circ$ was chosen as the optimum detection geometry for the following TR-XMCDR measurements. Static RMXD results of the AFM order are shown in Fig. 2(c, d). The photon energy scan (Fig. 2(c)) confirms the resonant behavior of the RMXD peak. The temperature-dependent $\theta$-2$\theta$ scans (Fig. 2(d)) confirm that the RMXD peak vanishes above 230 K and corresponds to the magnetic diffraction of the (0 0 0.5) AFM order, which is consistent with the previous report. The correlation length of the AFM order was estimated as ~30.5 nm by the peak width in Fig. 2(d), which is a little smaller than the film thickness possibly because of finite x-ray penetration depth or imperfections at the surface and interface. Photon energy was chosen at 778 eV for the TR-RMXD measurements.

Photo-induced AFM-FM transition. Since GBCO exhibits an AFM-FM transition with low-temperature AFM phase ($T_{AFM-FM}\sim230$ K) and high-temperature FM phase ($T_C\sim300$ K)\textsuperscript{15,19}, it can be expected that laser pumping can promote a transient FM state at temperatures below the AFM-FM transition, as observed in FeRh ($T_{AFM-FM}\sim375$ K, $T_C\sim680$ K)\textsuperscript{14}. This prediction was confirmed by our TR-XMCDR measurements shown in Fig. 3(a). At 150 K, the transient increase of XMCDR beyond the unpumped value can be clearly observed. At lower laser fluences, the XMCDR increases immediately after the laser illumination and reaches a maximum of ~150% of the unpumped XMCDR. At higher laser fluence of 12.32 mJ/cm$^2$, the XMCDR exhibits a fast decay followed by an increase of XCMDR beyond the unpumped value. Note that at 250 K (Fig. 3(b)), which is above the AFM-FM transition temperature, the increase of the XCMDR beyond the unpumped value was not observed, rather a normal fast demagnetization and a slow recovery appeared. This confirms the occurrence of a photo-induced AFM-FM transition in GBCO thin film. Interestingly, the reflectivity of the sample also exhibits significant decay-recovery behavior (Fig. 3(c, d)), inferring the concomitant change of electronic structure. On the other hand, the TR-RMXD results in Fig. 3(c) indicate that the (0 0 0.5) AFM peak exhibits a normal decay-recovery process. Above the AFM-FM transition temperature (250 K, Fig. 3(f)), since the AFM peak does not exist anymore, no pump effect upon RMXD was observed. It can be clearly observed in Fig. 4 that laser-pumping mainly modifies the RMXD signal at the Co resonance, confirming that the decay of the antiferromagnetism is directly related to the Co sites.

As mentioned before, there is still finite net magnetization thus XMCD signal in the AFM state of our GBCO film. On one hand, the AFM-FM transition could be understood as a continuous increase of the canting angle of Co moments in different AFM sublattices. At temperature below the magnetic transition, the Co moments are aligned antiferromagnetically with a canting angle to hold finite magnetization. The canting angle gradually change during the transition until the sublattice magnetization become parallel, which is featured by the disappearance of the AFM peak. In this picture the RMXD intensity represents the anti-parallel aligned component of the Co moments.
both AFM and FM phases have collinearly aligned magnetic moments. Temperature or laser excitation only changes the relative ratio between these two competing phases. In this case the RMXD intensity represents the fraction of the collinear AFM phase. One should be able to distinguish these two pictures if the measurement has higher spatial resolution. But with the present spot size of x-ray, it is difficult to discriminate them. Nevertheless, the microscopic physical picture does not influence our following discussions and conclusions.

Thus, it can be understood from the results in Fig. 3 that when the laser fluence is low, photo-induced AFM-FM transition occurs with the increase of net magnetization characterized by XMCDR and the decrease of the anti-parallel aligned component of Co moments characterized by the RMXD. When the laser fluence is as large as 12.32 mJ/cm$^2$, the fast decay of both XMCDR and RMXD could be attributed to a photo-induced demagnetization or other mechanisms, which will be discussed later. During the recovery process, GBCO first enters a more FM transient state and the XMCDR increases to a value above the unpumped value after ~1000 ps, as shown in Fig. 3(a).

The delay scans in Fig. 3 are fitted by a double-exponential function,

$$I(t) = I_1 \exp(-t/\tau_1) + I_2[1 - \exp(-t/\tau_2)]$$  \hspace{1cm} (1)$$

convolved with a 70-ps-wide Gaussian time-resolution function to estimate the timescales of the decay/enhancement and recovery.
processes. The fitted parameters are listed in Table 1. The decay processes are generally faster than the time resolution. The enhancement of XMCDR at fluences of 5.39 and 7.7 mJ/cm² occurs with a time constant of \( \tau_1 \approx 100 \) ps, which is significantly slower than the decay processes in other curves. The recovery processes of reflectivity and RMXD have similar timescales while the recovery of the XMCDR is significantly slower than that of the reflectivity and RMXD. This point will be explained in the following parts.

Possibility of photo-induced SST. To achieve a better understanding about the dynamic behaviors described above, we detailedly investigated the photon energy dependence of the transient XMCDR and reflectivity. Figure 5(a, b) show transient reflectivity and XMCDR spectra at a moderate laser fluence of 5.39 ml/cm². At delay = 100 ps (Fig. 5(a)), the pump effect is strongly photon energy dependent. In the energy range from 775 eV to 778 eV, the absolute value of XMCDR is enhanced by the pump laser. While in the energy range from 778 eV to 782 eV, the pump laser does the opposite effect. In contrast, at delay=1400 ps (Fig. 5(b)), the absolute value of XMCDR is enhanced by the laser-pumping in the whole energy range of Co \( L_3 \) resonance. Laser-fluence dependence of the pump effect on the XMCDR (normalized to the corresponding unpumped values) can be more clearly observed in Fig. 5(c, d). When the laser fluence is small (green curves), a pump-induced spectral weight transfer of XMCDR from higher energy to lower energy can be observed at delay=100 ps (Fig. 5(c)) and then the spectrum evolves into an overall positive pumping effect of XMCDR within the range of the Co \( L_3 \) resonance at delay=1400 ps (Fig. 5(d)). At higher laser fluences (blue and red curves), the increase of XMCDR is postponed by the decay process. The spectral weight transfer of XMCDR also infers a photo-induced electronic state transition. Delay-time-dependent transient reflectivity spectra shown in Fig. 5(e, f) can provide more insight. The pump effect of the reflectivity spectra is also strongly photon energy dependent. Laser-pumping causes an increase of reflectivity in the energy range from 776 eV to 777 eV and a decrease in the energy range near the resonance peak from 777 eV to 781 eV.

The spin-state of Co\(^{3+}\) in GBCO is still under debate. Previous reports state that the pyramidal Co ions are in either HS\(^{15,19}\) or LS\(^{20,21}\). Octahedral Co\(^{3+}\) undergoes SST at \(~350\) K and various types of SSTs were proposed, such as LS-HS\(^{19,20}\) or IS-HS\(^{21}\). Nevertheless, one consensus is that pyramidal Co ions have stable spin-states and the octahedral Co ions are relevant to the SST\(^{19}\). Thus it is reasonable to predict that laser pumping can affect the spin-state of the octahedral Co\(^{3+}\). Here we adopt the ideas of stable HS at the pyramidal sites and a LS-HS transition at the octahedral sites for the following discussion.

Now we argue that a photo-induced LS-HS transition at the octahedral Co\(^{3+}\) sites, as also reported previously in LaCoO\(_3\)\(^{29,30}\), likely occurs together with the AFM-FM transition. It is previously reported that in Co\(^{3+}\) perovskite oxides, when the population of HS octahedral Co\(^{3+}\) increases, the intensity at the peak of the Co \( L_3 \) resonance decreases and a smaller feature

![Fig. 4 Pump effects on energy and angular dependence of resonant magnetic x-ray diffraction (RMXD).](https://example.com/fig4)

**Table 1** Fitted parameters of the dynamics of x-ray magnetic circular dichroism in reflectivity (XMCDR), reflectivity (R) and resonant magnetic x-ray diffraction (RMXD).

| Temperature (K) | Measurement | Fluence (mJ/cm²) | \( I_1 \) | \( \tau_1 \) (ps) | \( I_2 \) | \( \tau_2 \) (ps) |
|---------------|-------------|-----------------|---------|----------------|---------|----------------|
| 150           | XMCDDR      | 5.39            | -0.280 | 101            | 0.281   | 3300           |
| 150           | R           | 5.39            | 0.00548| 3.12           | -0.00545| 1500           |
| 150           | RMXD        | 5.39            | 0.0110 | 2.94           | -0.0110 | 1700           |
| 150           | R           | 5.39            | 0.0250 | 2.92           | -0.0250 | 1700           |
| 150           | XMCDDR      | 7.7             | 0.0085 | 5.39           | -0.00899| 3430           |
| 150           | R           | 7.7             | 0.0180 | 8.44           | -0.0185 | 4340           |

\( I_1 \), \( I_2 \), \( \tau_1 \) and \( \tau_2 \) are parameters obtained by fitting the data in Fig. 3 by Eq. (1). \( I_1 \) and \( I_2 \) are the amplitude of the two dynamic components. \( \tau_1 \) and \( \tau_2 \) are the characteristic time of the two dynamic components.
increases at the lower energy side\textsuperscript{15,19}, which is consistent with the photo-induced change of transient reflectivity spectra reported here. At delay=100 ps, the similar direction of spectral weight transfer of XMCDR and reflectivity can be understood that HS Co\textsuperscript{3+} contributes more to the magnetization due to its larger magnetic moment. At delay=1400 ps, the XMCDR spectral weight shifts back to the unpumped position due to the recovery of spin-state at the octahedral sites. Another evidence of photo-induced electronic structure change is the inconsistent reaction speed of XMCDR and RMXD signals to the laser-pumping. If the pumping only changes the AFM canting angle or the AFM/FM ratio, the XMCDR should increase with the same speed as the RMXD decreases. Due to the finite energy-transfer efficiency between the electronic and the magnetic degrees of freedom, the slower increase of XMCDR is likely related to the change of AFM canting angle or the AFM/FM ratio, while the fast decay of RMXD seems to be dominated by the SST.

It is worth mentioning that photo-induced SST could not be predicated only by judging the spectral change of the reflectivity. There are other possible reasons for such spectral change, e.g. valence change\textsuperscript{31} or charge disproportionation\textsuperscript{29} of Co ions. But in GBCO we conclude that photo-induced SST is a most probable explanation for the observed spectral change. The photo-induced transitions in GBCO significantly differ from the temperature-triggered AFM-FM transitions and SSTs in similar perovskite cobaltates in the sense that transitions of both magnetism and electronic structure are involved simultaneously. Generally the AFM-FM transition and SST are separated by the difference of transition temperatures in cobaltates\textsuperscript{19}.

Another question should be addressed when discussing the fast decay of RMXD signal. The decrease of RMXD at early delay times, such as delay < 100 ps, should be mainly attributed to the SST, rather than the change of AFM canting angle or the AFM/FM ratio. The LS-HS SST enhances the local moment, thus the decrease of RMXD could only be understood with further insight of the magnetic structure of GBCO. Due to the strong neutron absorption of Gd, neutron diffraction results and the exact magnetic structure of GBCO are barely reported. Thus here we refer to previously reported magnetic structures of other REBaCo\textsubscript{2}O\textsubscript{4-x} (\(x \sim 5.5\), RE=Pr, Tb, etc.) systems\textsuperscript{16,32,33}, as

![Fig. 5 Energy dependence of the pump effect on reflectivity and x-ray magnetic circular dichroism in reflectivity (XMCDR).](image)

Reflectivity and XMCDR spectra at ((a) Delay=100 ps; (b) Delay=1400 ps). Normalized XMCDR and reflectivity spectra at different delay time ((c) XMCDR, 100 ps; (d) XMCDR, 1400 ps; (e) Reflectivity, 100 ps; (f) Reflectivity, 1400 ps). Curves in (c-f) are normalized to the corresponding unpumped values.
schematically shown in Fig. 6. Considering a full AFM unit cell of GBCO, there are 16 different Co sites (pyramidal sites 1-8 and octahedral sites 9-16). A full AFM unit cell consists of two magnetic sublattices (upper sublattice: sites 5-8 and 13-16; lower sublattice: sites 1-4 and 9-12). Here we assume that the moments align collinearly within each sublattice and lie in the $a$-$b$ plane (parallel to the film surface)\cite{15,16}. In the picture of AFM sublattice canting, the AFM-FM transition can be described by the decrease of the canting angle $\beta$ shown in Fig. 6. Note that additional structural modulation along $a$-axis\cite{15,16} makes the Co magnetic moment alternate along this direction, even though the adjacent Co ions have similar coordination environment. We also assume that the size of Co moments are identical for 4 groups of sites (group 1: sites 1,4,5,8; group 2: sites 2,3,6,7; group 3: sites 9,12,13,16; group 4: sites 10,11,14,15) in our following analysis. Here we calculate the change of RMXD and XMCDR signals during the continuous change of both the moment sizes at octahedral sites and the canting angle by using the following formula\cite{35} (with the above-mentioned assumptions and $\pi$-polarized incident beam, only the $\pi$-$\sigma$ channel contributes to the RMXD signal):

$$I_{\text{RMXD}} \propto \sum_{n=1}^{16} M_n \cos \psi_n \cos \theta \sin \beta n \frac{\gamma_n}{2}$$

$$I_{\text{XMCDR}} \propto \sum_{n=1}^{16} M_n \sin \psi_n$$

(2)

where $M_n$ is the moment size of the $n$th site, $\psi_n$ is the clockwise angle from $-b$ axis to the moment direction when looking along the $-c$ direction (for the upper sublattice $\psi_n = \pm (n/2 - \beta)$, for the lower sublattice $\psi_n = \pm (n/2 + \beta)$), $\theta = 32^\circ$ is the scattering angle, $Q = (0 0 0.5)$, and $\gamma_n$ is the atom coordinate of the $n$th site in the unit cell shown in Fig. 6. To reproduce the decrease of RMXD induced by SST at the octahedral sites, a larger increase of $M_{9,12,13,16}$ than $M_{10,11,14,15}$ is necessary. The laser pumping effects upon XMCDR due to the $\beta$-decrease and the $M_n$-increase compete with each other. We demonstrate in Fig. 7(a) that with certain change of $M_n$ and $\beta$, it is possible to qualitatively reproduce the fluorescence scans of XMCDR and RMXD at delay=100 ps (Fig. 7(b)). The fast decay of XMCRD at high laser fluence (Fig. 3(a), 12.32 mJ/cm$^2$) is also reproduced in the calculation, which may not only originate from the photo-induced demagnetization mentioned before. Note that although the calculation is conducted with the scattering plane of $a$-$c$ plane and magnetic field parallel to $a$, the result will be the same if the scattering plane is the $b$-$c$ plane and magnetic field is along $b$.
Now we can comprehensively describe the photo-induced dynamic behaviors of GBCO, as schematically shown in Fig. 6. Laser illumination significantly changes the electronic structure of GBCO thin film, which can be characterized by the reflectivity. At the same time, pump laser also induces an AFM-FM transition, which is featured by the increase of XMCD and decrease of the RMXD. The processes related to the magnetic degree of freedom can be interpreted as the change of either the AFM canting angle or the AFM/FM ratio. In Fig. 6 we are using the picture of AFM sublattice moment canting and the discussion should be analogous in the picture of phase separation. The system is first pumped into a FM state with more fraction of HS octahedral structure degrees of freedom. The results indicate significantly changes the electronic structure of GBCO thin film, which can be characterized by the reflectivity. 

Conclusions
To conclude, in this work we investigated the dynamics of both FM and AFM orders as well as the electronic structure in GBCO thin film by time-resolved synchrotron resonant x-ray scattering techniques. A photo-induced AFM-FM transition coupled with SST at octahedral Co$^{3+}$ sites was confirmed by comprehensive investigations of laser-fluence, delay-time, and photon-energy dependencies of the dynamic behaviors. The simultaneous contribution of moment alignment and spin-state change to the magnetism in the transient state gives rise to the dynamic behaviors of XMCD, reflectivity and RMXD. The measured laser-pumping effect is qualitatively consistent with calculation results by considering the detailed magnetic structure of GBCO. Our investigation presents a photo-induced AFM-FM transition in a strongly correlated oxide system and a new category of photo-induced phenomena involving both magnetic and electronic-structure degrees of freedom. The results indicate significant magnetism and electronic structure in strongly correlated systems, not only in static states but also in transient states and dynamic behaviors.

Methods
The TR-XMCD and TR-RMXD measurements were performed at beamline UE56/1-ZPM (FEMTOSPEX) of BESY II by using the setups shown in Fig. 1b). For TR-XMCD measurements, a circular-polarization with fixed circular polarization at the Co 2p-edge was used and an in-plane magnetic field of 1 T was switched to observe the magnetic contrast of the reflectivity. The incidence angle was fixed at 5°. The reflectivity was detected with an avalanche photodiode and boxcar integrated. For TR-RMXD measurements, we used horizontal linearly polarized x-ray (σ-polarization) instead to enhance the magnetic diffraction, with a constant in-plane magnetic field of 1 T applied. The diffraction signal was integrated via photon counting. A Tsapphire laser (λ=800 nm, σ-polarization, 3 kHz, pulse width ~ 50 fs) was employed as the pump source. The full width at half maximum (FWHM) spot sizes (horizontal x vertical) of the pump laser and the probe x-ray were around 0.34 × 0.38 mm$^2$ and 0.12 × 0.04 mm$^2$, respectively. The time resolution of the measurements was limited to ~70 ps by the pulse width of the probe x-ray. The pumped and unpumped signals were collected alternately by recording the contributions from the pumped and unpumped bunches. The sample temperature was controlled by a liquid N$_2$ flow cryostat. Since the measurement geometries of XMCD and RMXD were different, the surface-transmitted laser fluence was calibrated by measuring the incident-angle dependence of the laser power reflected by the sample surface. All the laser fluences mentioned below are calibrated fluences which are absorbed by the sample.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
H.W. and T.H. supervised the research and conceived the experiments. T.K. and A.C. prepared the GBCO film. Y.Z., C.S.-L., N.P., Y.H., K.T., K. Yamagami, K.I. and K. Yamamoto conducted the time-resolved synchrotron experiments. Y.Z. prepared the manuscript. All the authors contributed to the analysis of the results.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Yujun Zhang.

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