

学位論文

Nonlinear coherent spin dynamics in
antiferromagnets initiated
by Tesla-class terahertz magnetic fields

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Abstract

A good understanding of spin dynamics is essential for the design and development of a variety of spintronic devices for information transport, processing, and recording. In contrast to ferromagnets, antiferromagnets have the advantage of an intrinsic high-speed spin precession at terahertz (THz) frequencies as a result of the robust antiferromagnetic exchange interaction. Thus, ultrafast control of antiferromagnetic spins has attracted considerable interest. Initially, the use of circularly polarized near-infrared pulses emerged as a viable method for coherent spin excitation because an effective magnetic field can be generated through the inverse Faraday effect. Subsequently, alternative methods were discovered. For instance, it has been shown that the exchange interaction can be modified by exciting charge-transfer electronic transitions or lattice vibrations. However, these methods often lead to significant heating, because they strongly excite either electrons or phonons. Since 2010, the use of THz pulses (usually in the range of $0.1\text{--}3\times 10^{12}$ Hz) has emerged as a method for coherent spin excitation that does not involve a strong excitation of electrons or phonons, because these pulses have low photon energies. The feasibility of coherent spin excitation using THz electric fields has been demonstrated by resonantly exciting a crystal-field-split electronic transition within the ground-state doublet of a rare-earth ion in an orthoferrite. This method is limited to materials with crystal-field split transitions at THz frequencies as well as sufficiently low temperatures where a thermal population that hinders THz excitation is not created. The use of THz magnetic fields can be regarded as the most general method to coherently excite antiferromagnetic spins in various materials and temperature ranges. However, due to the relatively weak magnetic field of THz pulses propagating in free space, many experiments on nonlinear coherent spin dynamics in antiferromagnets can only investigate a restricted range of phenomena.

In this thesis, we present our investigations on the nonlinearities of the coherent spin dynamics in the rare-earth orthoferrites HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ near room temperature using Tesla-class THz magnetic fields. Both HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ are canted antiferromagnets with a small net magnetization. The spin dynamics in these antiferromagnets can be described in terms of their eigenmodes: the quasi-antiferromagnetic (q-AFM) and the quasi-ferromagnetic (q-FM) modes. The nonlinearities of the q-AFM mode in HoFeO_3 and the q-FM mode in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ were studied using the same experimental method: To generate a Tesla-class THz magnetic field in the sample, we designed a spiral-shaped microresonator and fabricated it on the sample surface by electron-beam lithography. When the microresonator is irradiated with a THz pulse, an oscillating current is induced that generates a strong multicycle THz magnetic near field perpendicular to the sample surface. The coherent spin dynamics initiated by the THz magnetic near field are detected by measuring the change in the ellipticity angle ($\Delta\eta$) of an 800-nm probe pulse due to the magneto-optic effect.

Firstly, in the case of HoFeO_3 , we chose a crystal orientation where the net magnetization is parallel to the magnetic near field to ensure that only the q-AFM mode is excited. The time-resolved magneto-optic signal $\Delta\eta$ showed an oscillation at about 0.58 THz, the frequency of the q-AFM mode. The following nonlinear phenomena were observed: (a) The upper and lower envelopes of the oscillation of $\Delta\eta$ become more asymmetric as the field strength is increased; apart from the fundamental peak at about 0.58 THz, the corresponding spectrum contains the second- and third-order harmonics, and their integrated peak areas obey a power law. (b) The q-AFM-mode frequency exhibits a redshift as the field strength is increased. We investigated the origins of these nonlinear phenomena by solving the Landau–Lifshitz–Gilbert (LLG) equation for

a two-sublattice model. We found that, under strong excitation conditions, the q-AFM mode cannot be approximated as a harmonic oscillator. The observation of the third-order harmonic clearly verifies the anharmonicity of the potential. Due to the sinusoidal potential, the frequency of the q-AFM mode exhibits a redshift as the field strength is increased. From the value of the redshift observed in the experiment, we estimated a maximum spin deflection angle of about 34 degrees away from the equilibrium orientation. The asymmetric envelopes and the second-order harmonic are attributed to the nonlinearities of the magneto-optic effect related to the q-AFM mode and can be reproduced well by the numerical solution of the LLG equation and the wave equation for the probe pulse propagating through the sample. These results reveal the nonlinearities of q-AFM modes in antiferromagnets.

Secondly, in the case of $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$, the magnetic near field (with a spectral peak at about 0.46 THz) forms an angle with the net magnetization that lies between 0 and 90 degrees, depending on the sample temperature. Above 310 K, the time-resolved magneto-optic signal $\Delta\eta$ showed a superposition of the q-FM (<0.05 THz) and the q-AFM (~ 0.5 THz) modes. We found the following behaviors: (a) As the field strength is increased beyond a critical value, a long-lived offset emerges after the first half cycle of the q-FM mode, and the amplitude of this offset exhibits a steep dependence on the field strength. (b) The offset changes drastically with the temperature, which controls the magnetic potential of the q-FM mode (we can control the barrier height between the two potential minima in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$); the offset only appears when the potential barrier is small enough. These two features of the offset reveal that spin switching occurs in this system after sufficiently strong excitation, that is, the magnetic order parameter overcomes the barrier and reaches the second potential minimum. We derived and solved the sine-Gordon equation based on the LLG equation to reproduce the q-FM-mode dynamics including the spin-switching phenomenon. This sine-Gordon equation includes the effect of the Zeeman torque directly exerted by the magnetic near field and that of coupling between the q-AFM and q-FM modes. To explain why the offset emerges after the first half q-FM-mode cycle, we analytically solved the sine-Gordon equation by replacing the expression for the potential modified by the fast-oscillating magnetic field with a “time-averaged” effective potential that varies with the envelope of the field. We found that the effective potential initially drives the magnetic order parameter away from the barrier, and when the potential modification vanishes, the magnetic order parameter starts to approach the barrier and overcomes it due to the inertia effect. These results clarify the nonlinearities of the q-FM mode in this antiferromagnet.

Finally, in this thesis, we summarize the nonlinear coherent dynamics of the q-AFM and q-FM modes in HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$, respectively. The observed frequency redshift and the third-order harmonic of the q-AFM mode reflect the anharmonic potential energy for the q-AFM mode. Regarding the q-FM mode, we observed an extremely nonlinear phenomenon, spin switching. The excitation process responsible for spin switching is an intriguing nonlinear process where a multicycle THz magnetic field modifies the potential for the q-FM mode. Similar processes can also occur in electron systems, and this type of control through multicycle fields is also known as Floquet engineering. Our investigations show that THz magnetic near fields are potentially useful for the investigation of coherent spin nonlinearities and novel methods for ultrafast manipulation of spin states.

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Chapter 1 Introduction

With advancements in laser technology, it is now possible to generate laser pulses with broadband wavelengths and various durations. The laser pulses can interact with different degrees of freedom within materials, including electrons, lattice structures, and spins. Strong excitation and nonlinear control of these elements open a new path for the ultrafast manipulations of the macroscopic properties of materials¹⁻³, which has been demonstrated in various electron and lattice systems, such as light-induced superconductivity^{4,5}, ferroelectricity^{6,7}, and edge states^{8,9}. Because the spin orders in the magnets exhibit nonvolatility and low dissipation, they are now widely used in the storage devices, and are expected as the potential information carrier in the next-generation devices¹⁰⁻¹². Therefore, the nonlinear control of spin orders is receiving more and more attention but have largely remained unexplored¹³⁻¹⁶. In this thesis, we investigate the ultrafast nonlinear control of spin orders in the antiferromagnets. The chapter 1 provides a general introduction of the spin dynamics in ferromagnets and antiferromagnets, and then reviews the previous studies on the ultrafast control of their magnetic properties using laser pulses at various wavelengths.

1.1 General theory of spin dynamics

Antiferromagnet is a magnetic material where spins are aligned antiparallel leading to a zero net magnetization. The antiferromagnetic ordering was first found by Louis Néel¹⁷ (pioneering work on this topic was honored with the Nobel Prize for Physics in 1970). The arrangement of these spins can be described by the spin sublattices. In each sublattice, all spins have the same direction. The spins between different sublattices are coupled with each other via the exchange interaction. In the simplest case, when the exchange interaction is negative, spins in different sublattices are aligned parallel to make the energy term minimum as shown in Fig. 1-1a, which leads to the ferromagnetic order. When the exchange interaction is positive, spins in

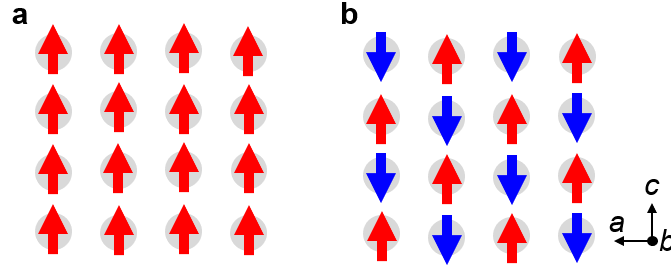


Figure 1-1. The schematic diagram illustrating the arrangement of spins in a ferromagnet (a) and an antiferromagnet (b).

different sublattices are aligned antiparallel leading to the antiferromagnetic order as shown in Fig. 1-1b.

One advantage of antiferromagnets is that the spin dynamics are at terahertz (THz) frequencies which is much faster than the spin dynamics in ferromagnet that is limited to gigahertz (GHz) frequencies. The spin dynamics in ferromagnets are determined by the external magnetic field with few-Tesla order, but in antiferromagnets, the frequencies of spin dynamics depend on the exchange interaction, which is about hundreds of Tesla. Because of the spin dynamics in the picosecond time scale, antiferromagnets are expected to be applied in spintronics and magnonics for ultrafast performance. Also, since antiferromagnets do not generate stray magnetic field, they can operate without cross-talk even when packed tightly, which is essential for the miniaturization of spintronics. In the following, we will discuss the frequency of spin dynamics more detail.

Firstly, we present the spin dynamics in ferromagnet. All spins are oriented at the same direction; thus, the collective spin dynamics can be described by the motion of a single macroscopic magnetic moment $\mathbf{M}$. The equation of motion was identified by Landau and Lifschitz in 1935¹⁸, and then a damping term was introduced by Gilbert in 1955. The complete equation is called Landau-Lifschitz-Gilbert (LLG) equation and is given by,

$$\frac{d\mathbf{m}}{dt} = -\gamma \mathbf{m} \times \mathbf{B}_{\text{eff}} + \alpha_{\text{LLG}} \mathbf{m} \times \frac{d\mathbf{m}}{dt}, \quad (1-1)$$

where γ is the gyromagnetic ratio which approximately equals to 1.76×10^{11} rad/(S⁻¹T⁻¹), and α_{LLG} is the Gilbert damping parameter (with positive value). The normalized magnetic moment is defined by $\mathbf{m} = \mathbf{M}/M_0$, where M_0 is the equilibrium value of $\mathbf{M}$. The equation describes a precession of $\mathbf{m}$ along a spiral path to the direction parallel with $\mathbf{B}_{\text{eff}}$. $\mathbf{B}_{\text{eff}}$ is given by the gradient with respect to $\mathbf{m}$ of the free energy F , $\mathbf{B}_{\text{eff}} = -\nabla F/M_0$. When there is no anisotropic interaction, the free energy F is given by, $F = -M_0 \mathbf{B} \cdot \mathbf{m}$, where $\mathbf{B}$ is the external magnetic field. The frequency of ferromagnetic resonance can be given by,

$$\nu_{\text{FMR}} = \frac{\gamma B}{2\pi}. \quad (1-2)$$

Because B normally is at few-Tesla orders, the ferromagnetic resonance is at GHz frequencies.

Secondly, because there are two different sublattices of spins in antiferromagnets, the collective spin dynamics can be described by the motions of two macroscopic magnetic moments, $\mathbf{M}_1$ and $\mathbf{M}_2$. The equations of motion are given by a set of LLG equations,

$$\frac{d\mathbf{m}_i}{dt} = -\gamma \mathbf{m}_i \times \mathbf{B}_{\text{eff},i} + \alpha_{\text{LLG}} \mathbf{m}_i \times \frac{d\mathbf{m}_i}{dt}, \quad (1-3)$$

where $i = 1$ or 2 is the index of sublattices and $\mathbf{m}_i$ is the normalized sublattice magnetizations $\mathbf{m}_i = \mathbf{M}_i/M_0$ (M_0 is the equilibrium value of $\mathbf{M}_1$ and $\mathbf{M}_2$). The effective magnetic field $\mathbf{B}_{\text{eff},i}$ is given by the gradient with respect to $\mathbf{m}_i$ of the free energy F , $\mathbf{B}_{\text{eff},i} = -\nabla_i F/M_0$. In the material with uniaxial anisotropy, the free energy F includes the exchange interaction H_E and one anisotropy interaction A_{cc} ,

$$F = H_E M_0 \mathbf{m}_1 \cdot \mathbf{m}_2 - A_{cc} M_0 (\mathbf{m}_{1c}^2 + \mathbf{m}_{2c}^2) - M_0 \mathbf{B} \cdot (\mathbf{m}_1 + \mathbf{m}_2), \quad (1-4)$$

The frequency of antiferromagnetic resonance without external magnetic field can be obtained¹⁹,

$$\nu_{\text{AFMR}} = \frac{\gamma}{2\pi} \sqrt{4H_E A_{cc} + 4A_{cc}^2} \quad (1-5)$$

Because H_E usually has hundreds of Tesla and A_{cc} has few of Tesla, the antiferromagnetic resonance is at the THz frequencies. The spin precession at frequency ν_{AFMR} have two opposite directions (left-hand precession and right-hand precession), and thus are degenerate. The degeneracy can be lifted by an external magnetic field or an additional anisotropy interaction.

The materials used in our experiments are rare-earth orthoferrites which are typical canted antiferromagnets. There are two uniaxial anisotropy interactions (a axis and c axis) and a Dzyaloshinskii-Moriya interaction. The Dzyaloshinskii-Moriya interaction prefers spins to align in a - c plane, and slightly cants the antiparallel spins thus leading to a small net magnetization as shown in Fig. 1-2. Due to these anisotropy interactions, the material has two nondegenerate eigenmodes of spin dynamics: quasi-antiferromagnetic (q-AFM) mode and quasi-ferromagnetic (q-FM) mode. Besides, the anisotropy interaction along a axis is a function of temperature and leads to a phase

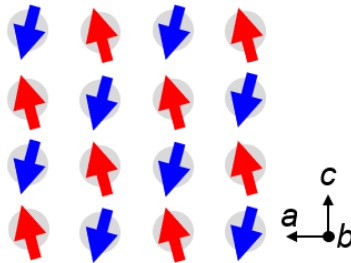


Figure 1-2. The schematic diagram illustrating the arrangement of spins in a canted antiferromagnet.

transition called spin reorientation transition (SRT) in a specific temperature range, where, as temperature increases, the easy axis of spins rotates continuously from c axis to a axis.

For the ultrafast manipulation of spin orders, ultrashort laser pulses are employed to drive them into nonequilibrium states, as shown in Fig. 1-3. The mechanisms rely on both direct and indirect interactions. The direct interaction occurs between the spins and the magnetic components of the laser pulses via Zeeman torque. Indirect interaction involves the spins and the electric components of the laser pulses, mediated by spin-orbit or exchange interactions. Various excitations of electrons and lattices can modify the orbital states, hopping rates, or wave-function overlaps, which leads to the modifications of the spin-orbit or exchange interactions. we will review these studies on ultrafast control of spins in the canted antiferromagnets in the following sections.

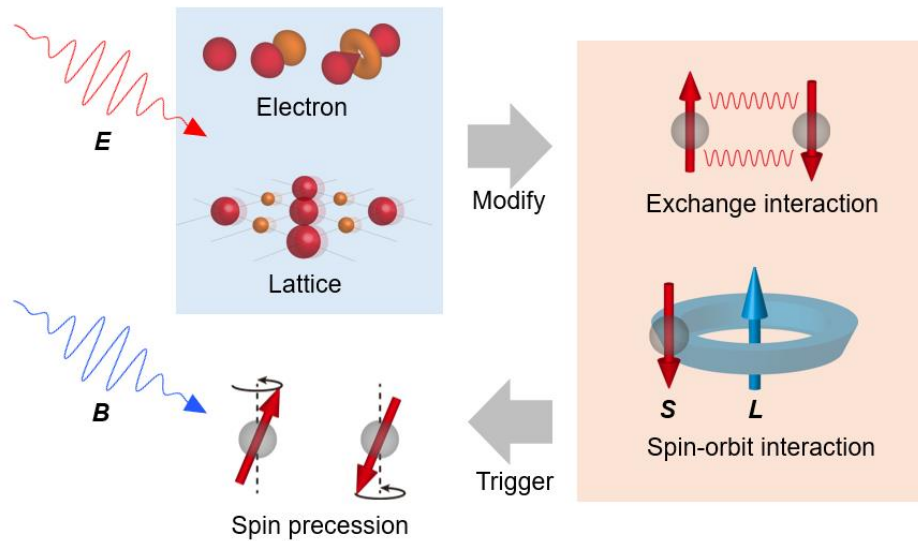


Figure 1-3. The schematic diagram illustrating the control methods of spin orders. The magnetic components of laser pulses excite the spin dynamics directly, and the electric components excite the spin dynamics via the interactions with electron and lattice.

1.2 Ultrafast control of antiferromagnetic spin dynamics using optical pulses

1.2.1 Heating effect

In the pioneering work, the ultrafast control of spin orders is realized by impinging heat into Ni film with laser pulses²⁰ where the temperature increasing homogenizes the majority and minority spins leading to a demagnetization. Then the group Kimel et al. utilized the same method in a canted antiferromagnet²¹, TmFeO₃, which is one of the rare-earth orthoferrites. In the material TmFeO₃, the anisotropy interaction that plays a determinative role in the direction of spins varies with temperature. In that experiment, the near-infrared (NIR) laser pulse excited the electron states of rare-earth and iron ions and thermalize the lattice through electron-phonon scattering in 0.3 ps. This leads to the changes of the anisotropy interaction and thus the potential energy. During the process where spins relax to the new minimum of the thermalized potential energy (the process is called spin reorientation), the spin

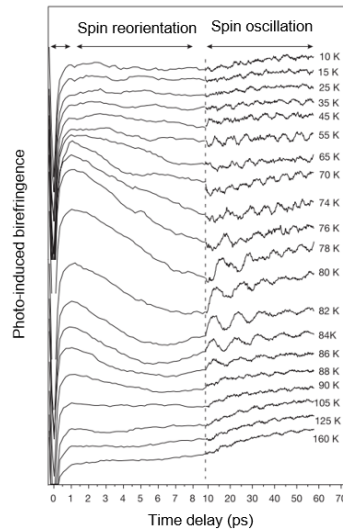


Figure 1-4. Heat-induced spin dynamics in rare-earth orthoferrite TmFeO₃. The temperature increase modifies the potential energy, thus creating a new potential minimum. The relaxation to the new minimum leads to the spin reorientation, and the subsequent spin oscillation. Figure reprinted with permission from the reference²¹, © 2004 Springer Nature.

1.2 Ultrafast control of antiferromagnetic spin dynamics using optical pulses

oscillations are excited, and observed in the picosecond time scales as shown in Fig. 1-4.

1.2.2 Inverse Faraday effect

The thermal method to excite the spin dynamics has been demonstrated. However, because the cooling of temperature to equilibrium is very slow, it hinders the application at a high repetition rate. The group Kimel et al. thus developed a nonthermal method based on the inverse Faraday effect (IFE). The irradiation of circularly polarized light can induce a static magnetization along the propagation direction via the spin-orbit interaction, which is similar with an external magnetic field. This is a Raman-like optical scattering not involved in the optical absorption, and thus is non-thermal. The method is first demonstrated in the work²² with DyFeO₃ where the circularly polarized NIR pulses induces ultrafast spin deflections, as shown in Fig. 1-5a. During the process of spins relaxing to the equilibrium, spin oscillation is excited. Because the NIR pulses with opposite helicities deflect spins towards opposite directions, the oscillations exhibit opposite phases.

In the follow-up study, it is demonstrated that a spin switching can be

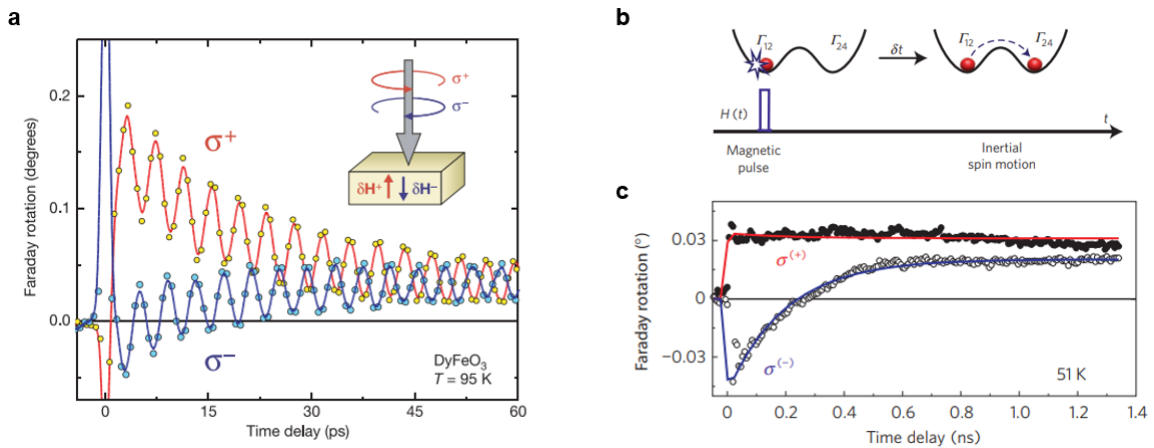


Figure 1-5. a, Spin dynamics excited by IFE in rare-earth orthoferrite DyFeO₃. Figure reprinted with permission from the reference²², © 2005 Springer Nature. **b,** The schematic of spin switching driven by an ultrashort laser pulse via IFE. **c,** Experimental results of spin switching realized in rare-earth orthoferrite HoFeO₃. Figure reprinted with permission from the reference²³, © 2009 Springer Nature.

1.2 Ultrafast control of antiferromagnetic spin dynamics using optical pulses

induced²³ in HoFeO_3 crystal. As the temperature is set in the temperature range of SRT, the potential energy exhibits tunable double minima. The circularly polarized laser pulses impact the impulsive force onto the spins and thus trigger the spin switching between the double minima as shown in Figs. 1-5b and c. The offsets before 0.1 ns which depend on the helicity are the evidence of the spin switching. After 0.1 ns, the influence of heating effect emerges and erases the offset induced by spin switching. The heating effect lasting tens of nanoseconds is induced by the thermalization between the lattice and the excited electrons. Although IFE does not require the real excitation of electrons, it cannot be avoided due to the finite absorption of photons at NIR wavelengths which results in heating effects.

1.2.3 Coupling to electron or lattice

After the work²² by Kimel et al. in 2005, numerous studies on the nonthermal excitation of spin dynamics have emerged²⁴⁻²⁷. In these studies, the electrons or lattices are strongly excited by laser pulses. As a result, the couplings between spins and electrons or lattices phenomenally generate transient torques and thus trigger the spin dynamics. In the following, the couplings are discussed in detail.

Firstly, a type of the coupling between electrons and spins is introduced²⁴. In the rare-earth orthoferrites, the superexchange interactions between iron ions are mediated by the oxygen ions and happen due to the virtual hopping of electrons between the iron and oxygen ions. Hence, they anticipated that the optical excitation of the electron distributions can transiently modify the superexchange interaction and thus generate the torque to trigger spin dynamics. Mikhaylovskiy et al. performed the experiment to demonstrate the prediction by exciting the charge-transfer transition in TmFeO_3 with NIR pulses and monitoring the THz emission generated by the spin dynamics²⁴ as shown in Fig. 1-6. Furthermore, there is another coupling between spins and electrons accessible for excitation of spin dynamics in the rare-earth orthoferrites (for

1.2 Ultrafast control of antiferromagnetic spin dynamics using optical pulses

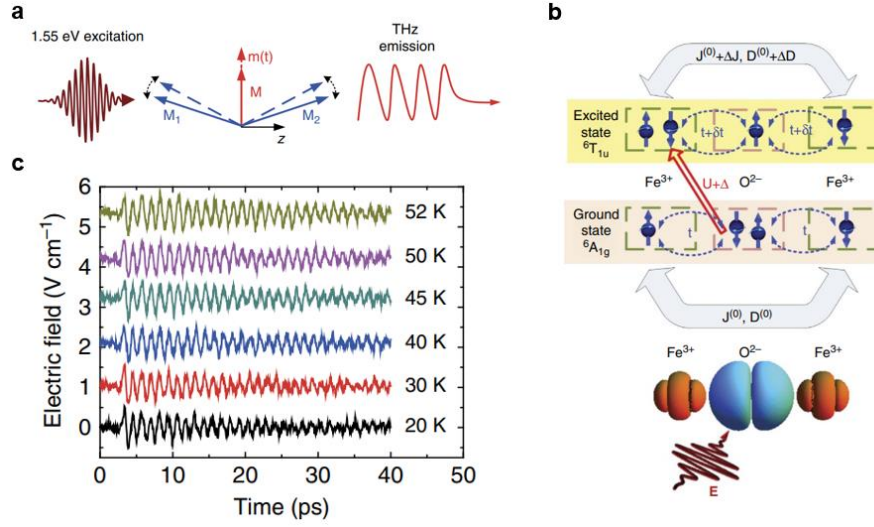


Figure 1-6. **a**, Schematic of experiment where spin dynamics are excited by NIR pulses and are detected by monitoring THz emission. **b**, The optical transition (thick red arrow) from the ground state to the excited state. In the ground state, the exchange interactions $J^{(0)}$ and $D^{(0)}$ between iron ions are mediated by the hopping t (dashed blue double arrows) of electrons (blue balls with arrows indicating spins) between iron and oxygen ions. **c**, Experimental results of spin dynamics in rare-earth orthoferrite TmFeO₃. Figure reprinted with permission from the reference ²⁴, © 2015 Springer Nature under the terms of the Creative Commons CC BY license.

example, Sm_{0.7}Er_{0.3}FeO₃,²⁶): the excitation of the 4*f* electrons of rare-earth ions can modify the anisotropy interactions between the rare-earth ions and the iron ions²⁶.

Secondly, the coupling between spins and lattices is introduced. The overlaps of electronic wave functions between rare-earth and iron ions determine the anisotropy interactions. The excitation of phonon modes can modify the distances between rare-earth and iron ions, thus modulating the overlaps of wave functions and the anisotropy interactions, as shown in Fig. 1-7a. Afanasiev et al. investigated the control of spin orders²⁷ by exciting the phonon modes using mid-infrared (MIR) pulses in a rare-earth orthoferrite DyFeO₃. They found that when the intensity of laser pulses exceeds the threshold, spin switching can be triggered, which can be confirmed by the amplitude of signal ΔM shown in Figs. 1-7b and c. The increase of ΔM becomes steeper when the pump intensity increases beyond the threshold. However, similarly as the

1.2 Ultrafast control of antiferromagnetic spin dynamics using optical pulses

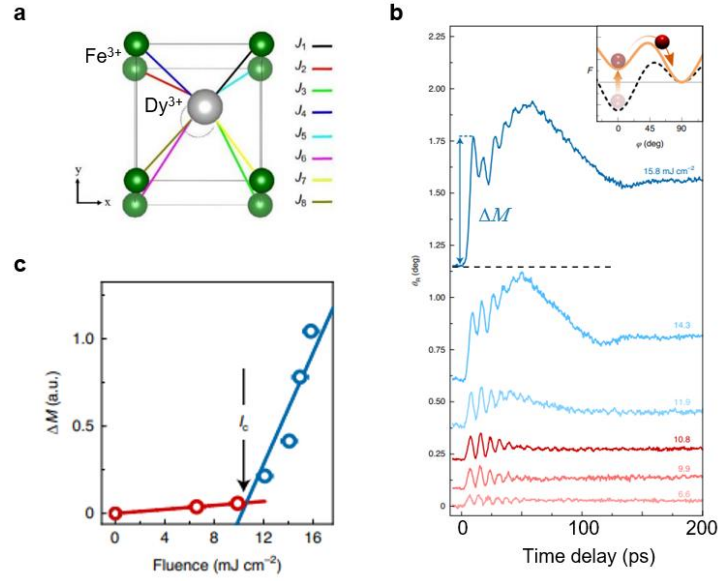


Figure 1-7. a, Lattice distortion induced by phonon excitation in rare-earth orthoferrite, DyFeO_3 . The colorful lines refer to the anisotropy interactions between iron and rare-earth ions. **b,** The spin switching driven by an ultrashort MIR pulse where the deviation of macroscopic spin order from equilibrium is defined by ΔM . **c,** Dependence of ΔM on pump intensity. The threshold of spin switching is indicated. Figure reprinted with permission from the reference²⁷, © 2021 Springer Nature.

excitation via IFE, the heating effect emerges and erases the result of spin switching after 100 ps (the potential energy is changed by the increase of temperature, and thus the potential minima become different from the equilibrium state).

In this section, we introduced various nonthermal methods for ultrafast manipulation of spin orders using optical pulses in the range from NIR to MIR frequencies. However, these methods use light with high photon energy and thus it is unavoidable to excite electrons or phonons even without intention. Due to the thermalization between electron and lattice, the temperature increases, leading to the undesired modification of potential energy. Because the cooling of temperature to equilibrium is very slow, it limits the high-speed application. There is a demand to excite the spin dynamics with much less heating effect.

1.3 Ultrafast control using the magnetic fields of THz pulses

As the development of THz technology, the electric components of THz pulses were used to excite the elementary excitation in solids, such as phonon, cyclotron, exciton and cooper pair. Because the resonances of spin dynamics in antiferromagnets lie in the THz range, THz pulses were considered to be potential for the ultrafast manipulation of antiferromagnetic spin orders. It was first demonstrated by Yamaguchi et al.²⁸ They exploited the impulsive Zeeman torque applied by the magnetic component of THz pulse to resonantly drive the spin dynamics as shown in Fig. 1-8, where two eigenmodes of spin dynamics can be observed in the sample of YFeO₃. The double pulses here were used to selectively induce the destructive interference of one mode. In the almost transparent materials at THz frequencies, THz pulses cannot be absorbed and thus can purely excite spins without excitations of other degrees of freedom. However, the THz magnetic field in free space is too weak (up to ~ 0.1 T even with the regenerative amplified laser pulses^{29–31}) to excite spin dynamics into a nonlinear regime.

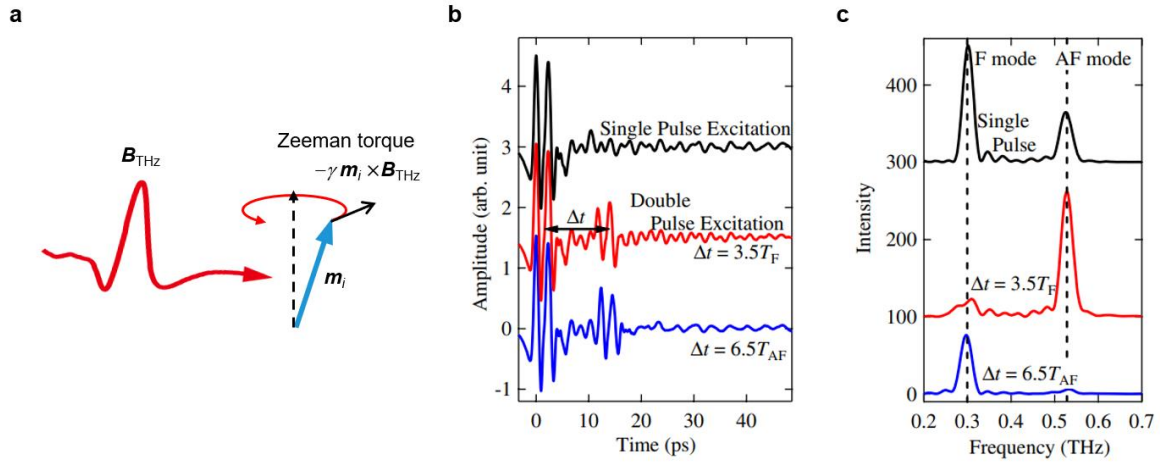


Figure 1-8. **a**, Zeeman torque applied by the magnetic component of the THz pulse is shown by the solid black arrow. Sublattice magnetization $\mathbf{m}_i$ in antiferromagnet is perturbed out of the equilibrium (dashed black arrow) and starts to precess (thin red arrow). **b**, The temporal development of spin dynamics driven by THz pulses in rare-earth orthoferrite YFeO₃ is shown. **c**, Corresponding spectra of the data in **b**. Figure reprinted with permission from the reference²⁸, © 2010 American Physical Society.

1.4 Ultrafast control using the electric fields of THz pulses

Baierl et al. turned to exploit the THz electric pulse to drive spin dynamics³² in rare-earth orthoferrite TmFeO_3 . In TmFeO_3 , the anisotropy interaction is determined by the electron distribution within the crystal-field-split ground states of rare-earth ions, because the different orbital angular moment of each split state is coupled to the spins of iron ions by exchange and dipole interactions. The thermal population of these states leads to the temperature dependence of anisotropy interaction and induces the spin reorientation transition. The energy separations between these split states in TmFeO_3 are around 1 THz, and thus the resonant excitation of the optical transition within the split ground states using THz pulses is one of the most efficient methods to

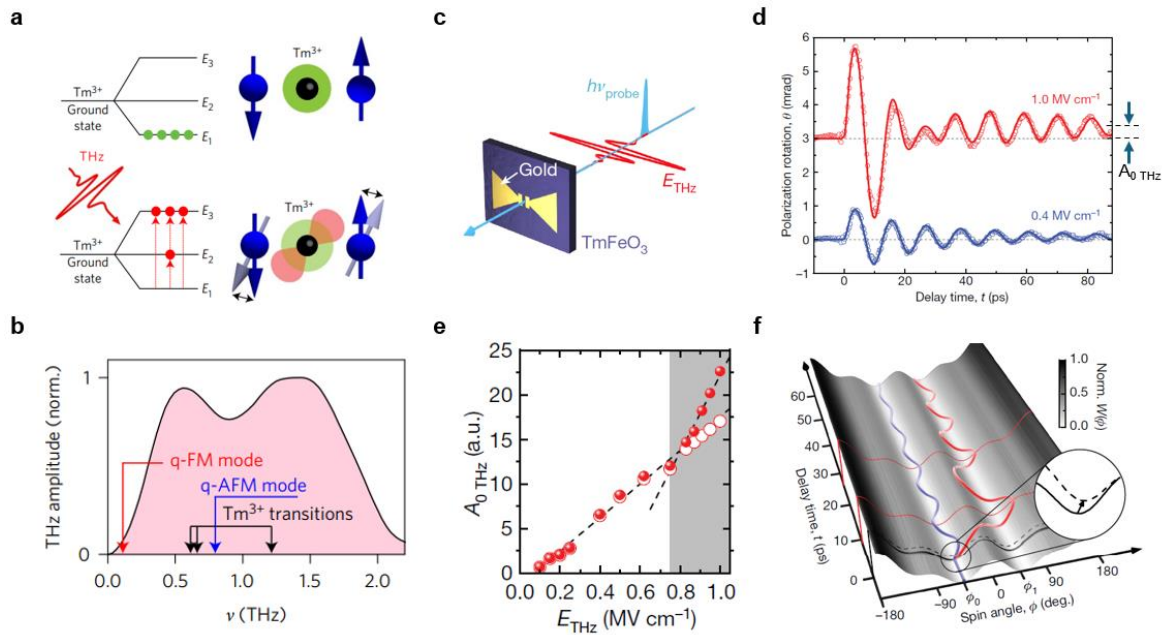


Figure 1-9. **a**, The crystal field splits the ground state of Tm^{3+} into several energy levels. The green shadow around Tm^{3+} refers to the orbital wave function. The blue arrows are spins of iron ions. **b**, The photon frequencies required for the resonant excitation of the optical transition within these states are indicated by the black arrows. Figure reprinted with permission from the reference³², © 2016 Springer Nature. **c**, The microscopic antenna is used to enhance the THz electric field. The blue line is the probe beam for the detection of spin dynamics. **d**, The offset is indicated by $A_0 \text{ THz}$. **e**, The field-strength dependence of $A_0 \text{ THz}$. **f**, The trajectories of spin dynamics. The red curve is the trajectory of spin switching. Figure reprinted with permission from the reference³³, © 2019 Springer Nature.

modify the anisotropy interaction (Figs. 1-9a and b). The transient modification triggers the spin dynamics. When the THz electric field is strong enough, which is realized by the local enhancement with a metallic antenna structure on the micrometer scale (Fig. 1-9c), the THz electric field can induce spin switching³³. As shown in Fig. 1-9d, the signal presents a long-lived offset $A_{0\text{ THz}}$. The offset in the weak-excitation regime ($E_{\text{THz}} < 0.75 \text{ MV cm}^{-1}$ as shown in Fig. 1-9e) is because that the excited electron distribution persists for a long time leading to a displacive change of potential energy. When the THz electric field becomes strong enough, the increase of the offset becomes steeper indicating an occurrence of spin switching. The trajectory of spin switching is shown in Fig. 1-9f. As shown by the inset, the THz electric field generate an impulsive change to the potential energy. The impulsive change functions as a torque to drive spins move towards the barrier between the double minima. If the impulsive change is strong enough, spins can overcome the barrier and relax to another potential minimum.

However, this method is limited by two points: Firstly, the material should have the electronic orbital transitions at THz frequencies. In rare-earth orthoferrites, the sort of rare earth determines the frequency. Secondly, the temperature should be low enough to suppress the thermal population of the crystal-field-split ground states, because the thermal population hinders the THz excitation. Therefore, for ultrafast manipulation of spin orders in various materials and temperature ranges, the strong excitation using THz magnetic fields is essential but has not been explored.

1.5 Purpose of this thesis and outline

The use of Zeeman torque applied by THz magnetic fields can be regarded as the most general method to coherently excite antiferromagnetic spins in various materials and temperature ranges. However, due to the relatively weak magnetic field of THz pulses propagating in free space, many experiments on nonlinear coherent spin dynamics in antiferromagnets can only investigate a

restricted range of phenomena.

In this thesis, we designed a spiral-shaped microresonator and fabricated it on the sample surface by electron-beam lithography. When the microresonator is irradiated with a THz pulse, an oscillating current is induced that generates a Tesla-class multicycle THz magnetic near field perpendicular to the sample surface. We use the strong THz magnetic near field to study the nonlinear spin dynamics in the canted antiferromagnets near room temperature.

The spin dynamics of canted antiferromagnet have two eigenmodes called q-AFM and q-FM modes. Each mode can be described by a motion equation with a magnetic potential energy. Firstly, we studied the nonlinearities behavior of spin dynamics in the potential energy of q-AFM mode: the frequency redshift, the second- and third-order harmonic generation and the asymmetric oscillation waveform of q-AFM mode are observed for the sample of HoFeO_3 . We revealed that the anharmonicity of potential energy plays a crucial role in these nonlinear phenomena. Secondly, we studied the spin switching in the potential energy of q-FM mode for the sample of $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$, where the magnetic order parameter moves from one potential minimum into another. We observed that the q-FM mode is non-resonantly excited, and under the strong excitation, spin switching happens after the first half cycle of the q-FM mode. This phenomenon is attributed to the dynamically construction of an effective q-FM-mode potential energy by the strong and multicycle magnetic pulse.

The chapters in this thesis are organized as follows:

Chapter 2 introduces the properties of rare-earth orthoferrites (HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$). The basic equations and the eigenmodes of spin dynamics in the materials are described in detail.

Chapter 3 introduces the experiment setup for the generation of THz pulses and the detection of spin dynamics. The properties of THz resonators for the generation of strong near fields are discussed.

Chapter 4 presents the first topic of nonlinear spin dynamics in HoFeO_3 crystal. The observed nonlinearities of q-AFM mode are discussed based on the

theoretical analysis using the motion equation of q-AFM mode with an anharmonic potential energy.

Chapter 5 exhibits the second topic of spin switching in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ crystal. The observed spin switching is discussed based on the theoretical analysis using the motion equation of q-FM mode. In the analysis, the time-period potential energy during the strong and multicycle magnetic field is replaced with a “time-averaged” effective potential that varies with the envelope of the field.

Chapter 6 summarizes the conclusions of the thesis.

Chapter 2 Sample

In this chapter, the fundamental physical properties of our antiferromagnetic samples, HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$, are introduced. Both samples are the rare-earth orthoferrites which belong to a type of charge-transfer oxide insulator. They are almost transparent at about 800 nm. The spins of iron ions contribute to the antiferromagnetism, where the neighboring spins are aligned antiparallel due to the superexchange interaction and are slightly canted by the Dzyaloshinskii-Moriya interaction. The competition between anisotropy energies along different axes leads to the spin-reorientation phase transition. The spin precessions in the canted antiferromagnets have two eigenmodes, the q-FM and q-AFM modes, whose frequencies are located in the low terahertz range (below 0.6 THz). The spin dynamics are detected by 800-nm probe pulses based on the Magneto-optic effect. The nonlinearities of the two eigenmodes are studied in this dissertation.

2.1 Crystal structure and optical properties

In this section, the crystal structure and optical properties of our samples are introduced. In our experiments, we used two rare-earth orthoferrites RFeO_3 ($\text{R} = \text{Ho}$ and $\text{Sm}_{0.7}\text{Er}_{0.3}$). The material RFeO_3 has the orthorhombic distorted perovskite structure belong to the space group Pbnm . As shown in Fig. 2-1, one Fe^{3+} ion is surrounded by six O^{2-} ions forming an octahedral FeO_6 cluster, which constitutes a framework of the perovskite structure. The rare-earth ions R^{3+} exist at the center of a unit cell which consists of four FeO_6 clusters. The octahedral is distorted due to the presence of a R^{3+} ion³⁴. The degree of distortion from cube perovskite increases with the atomic number of the rare-earth ion.

Because the electron transition of the common FeO_6 clusters plays an important role in the optical absorption, materials RFeO_3 with different R have

very similar optical spectra in the range from visible to near infrared regions³⁵. The optical absorptions are mainly contributed by the local electron transitions which are correlated to the local 3d orbital of Fe^{3+} . Therefore, the optical properties can be discussed qualitatively based on the electron state of one FeO_6 cluster.

The optical spectra of rare-earth orthoferrites, with $R = \text{Sm}, \text{Ho}$ and Er , are shown in Fig. 2-2. (The spectra for other kinds of R can be found in ref³⁵.) Apart from fine structures which are attributed to the rare-earth $4f \rightarrow 4f$ transitions³⁶,

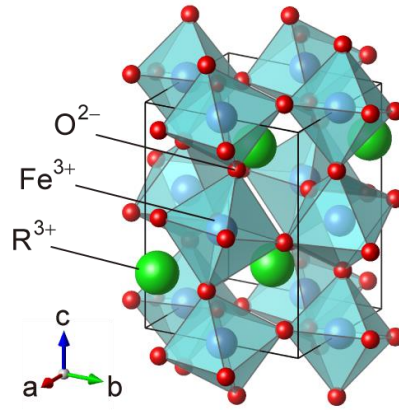


Figure 2-1. Crystal structure of the rare-earth orthoferrite RFeO_3 which is drawn using VESTA, © 2006-2024, Koichi Momma and Fujio Izumi. The license can be found at <<https://jp-minerals.org/vesta/en/download.html>>, accessed 20 June 2024.

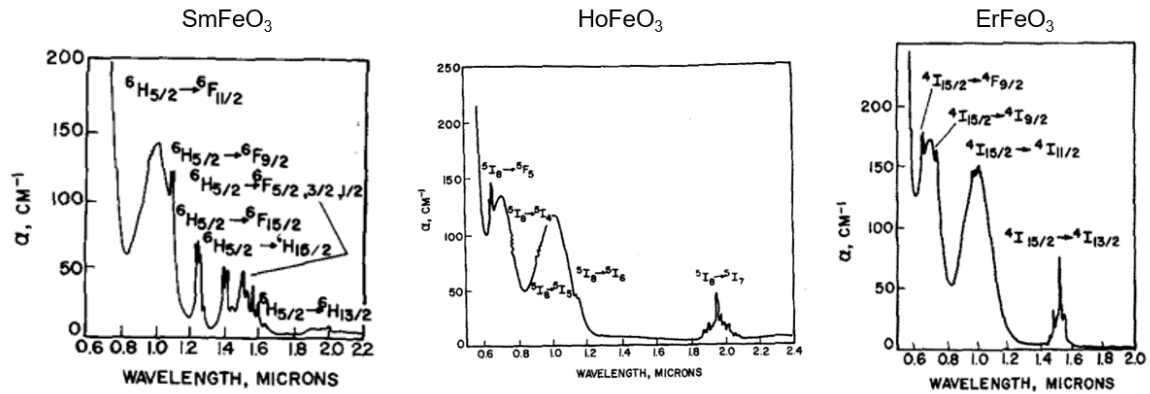


Figure 2-2. Absorption spectra of the rare-earth orthoferrites RFeO_3 at room temperature reported by the previous study. Figure reprinted with permission from the reference³⁵, © 1970 AIP Publishing.

there are mainly three absorption peaks for most RFeO_3 . The peaks at $0.7 \mu\text{m}$ and $1 \mu\text{m}$ are due to the crystal-field $d-d$ transitions of Fe^{3+} , ${}^6A_1 \rightarrow {}^4T_2$ and ${}^6A_1 \rightarrow {}^4T_1$, respectively. Besides, a strong absorption peak $> 0.5 \mu\text{m}$ can be observed. It is attributed to the charge-transfer transition³⁷ where the charges transfer from the $2p$ orbitals of O^{2-} to the $3d$ orbitals of Fe^{3+} . The dips at $0.8 \mu\text{m}$ between two $d-d$ transitions allow us to perform the magneto-optic measurements in a transmission configuration in thin samples of RFeO_3 (for $\text{R} = \text{Sm}, \text{Ho}, \text{Er}$).

2.2 Static magnetic properties

In this section, the magnetic properties of our samples at equilibrium are introduced based on the two-sublattice model. The free energy is used to describe the spin configuration and the spin reorientation transition.

2.2.1 Spin configuration

In RFeO_3 ($\text{R} = \text{Ho}$ and $\text{Sm}_{0.7}\text{Er}_{0.3}$) crystals, R^{3+} and Fe^{3+} are the magnetic ions. Near room temperature, the spins of R^{3+} are disordered and thus are paramagnetic. The magnetizations of the crystals are determined by the spins of $3d^5$ electrons of iron ions.

The spins are aligned antiparallel due to the nearest-neighbor superexchange interaction between spins of iron ions mediated by an oxygen ion. The model of two sublattice were used to describe the macroscopic magnetic properties. In each sublattice, spins are aligned in the same direction. The spins in different sublattices are aligned antiparallel. The normalized free energy of RFeO_3 ($\text{R} = \text{Ho}$ or $\text{Sm}_{0.7}\text{Er}_{0.3}$) is given by³⁸⁻⁴¹,

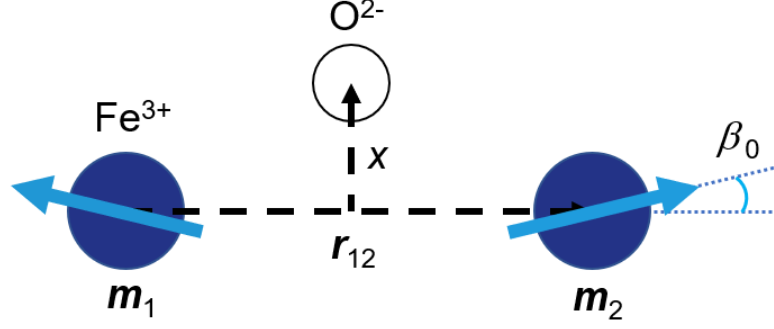


Figure 2-3. The configuration of three-ion $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ cluster.

$$\begin{aligned}
 V = & -\mathbf{B} \cdot (\mathbf{m}_1 + \mathbf{m}_2) + H_E \mathbf{m}_1 \cdot \mathbf{m}_2 + \mathbf{H}_D \cdot (\mathbf{m}_1 \times \mathbf{m}_2) \\
 & -A_{aa}(m_{1a}^2 + m_{2a}^2) - A_{cc}(m_{1c}^2 + m_{2c}^2) \\
 & + A_4(m_{1a}^4 + m_{1b}^4 + m_{1c}^4 + m_{2a}^4 + m_{2b}^4 + m_{2c}^4), \quad (2-1)
 \end{aligned}$$

where $\mathbf{m}_i (i = 1, 2)$ are the normalized sublattice magnetizations and $\{a, b, c\}$ refers to the crystallographic frame.

The first term is the Zeeman energy induced by external magnetic field $\mathbf{B}$, and is set to 0 in this section. The second term here is the superexchange interaction and H_E is a positive constant. To lower the free energy, $\mathbf{m}_1$ and $\mathbf{m}_2$ should be aligned antiparallel, leading to the antiferromagnetism. Therefore, H_E is also called antiferromagnetic exchange interaction. Because the term does not change when $\mathbf{m}_1$ and $\mathbf{m}_2$ are exchanged, it is a symmetric interaction.

The third term is the Dzyaloshinskii-Moriya interaction (DMI)^{42,43}, which appears by including the spin-orbital interaction in the calculation of the superexchange interaction. Because the sign is reversed when $\mathbf{m}_1$ and $\mathbf{m}_2$ are exchanged, it is an asymmetric interaction. The parameter $\mathbf{H}_D$ is given⁴⁴ by $\mathbf{H}_D \propto \mathbf{r}_{ij} \times \mathbf{x}$, where $\mathbf{r}_{ij}$ and $\mathbf{x}$ are defined in the Fig. 2-3. This expression indicates that if the iron ions and oxygen ions were in line, DMI would vanish. In RFeO_3 , the distortion of the orthorhombic perovskite structure induced by the rare-earth ions leads to the nonzero DMI. For orthoferrites in this literature, $\mathbf{H}_D$ is along b axis and thus,

$$\mathbf{H}_D \cdot (\mathbf{m}_1 \times \mathbf{m}_2) = H_D(m_{1c}m_{2a} - m_{1a}m_{2c}). \quad (2-2)$$

Due to the nonzero DMI, the antiparallel spins are canted leading to weak ferromagnetism as shown in Fig. 2-3. The equilibrium position of $\mathbf{m}_1$ and $\mathbf{m}_2$ are determined by finding the minimum of free energy, $\partial^2 V / \partial \mathbf{m}_i^2 = 0$. Under zero external magnetic field, the cant angle is given by, $\tan 2\beta_0 = H_D / (H_E + A_{aa} - A_{cc})$, where β_0 is about 0.6° near room temperature. Because H_E and H_D are temperature independent, the cant angle of sublattice spins almost do not vary with temperature. Due to the finite cant angle, the material is called canted antiferromagnet. The values of these parameters are obtained from various experiments^{40,45} and are estimated to be $H_E \sim 640$ T, $H_D/H_E \sim O(10^{-2})$, $A_{aa,cc}/H_E \sim O(10^{-4})$ and $A_4/H_E \sim O(10^{-5})$.

2.2.2 Spin reorientation transition

In Eq. (2-1), A_{aa} and A_{cc} are the anisotropy interactions which orient $\mathbf{m}_1$ and $\mathbf{m}_2$ to lie preferentially in a - c plane as shown in Fig. 2-4. The competition between A_{aa} and A_{cc} determines the easy axis of spins, thus leading to SRT. A_4 is the fourth-order anisotropy interaction and far smaller than A_{aa} and A_{cc} . Among these parameters, A_{aa} and A_4 are temperature independent, but A_{cc} depends on temperature.

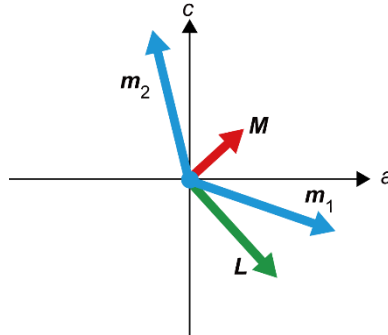


Figure 2-4. The configuration of sublattice magnetizations $\mathbf{m}_1$, $\mathbf{m}_2$, ferromagnetic vector $\mathbf{M}$ and antiferromagnetic vector $\mathbf{L}$ in the crystallographic frame $\{a, b, c\}$.

SRT is described in the following. At low temperature, $A_{cc} \gg A_{aa}$ (> 0), $\mathbf{m}_1$ and $\mathbf{m}_2$ are aligned antiparallel (little canted) in c axis. The configuration where the antiferromagnetic vector $\mathbf{L} = (\mathbf{m}_1 - \mathbf{m}_2)/2$ is along c axis and the ferromagnetic vector $\mathbf{M} = (\mathbf{m}_1 + \mathbf{m}_2)/2$ is along a axis, is marked by the symbol $\Gamma_2(L_c, M_a)$. When temperature increases, A_{cc} decreases and finally satisfies $A_{cc} \ll A_{aa}$, as a result, $\mathbf{m}_1$ and $\mathbf{m}_2$ rotate from c axis to a axis which is described by the symbol $\Gamma_4(L_a, M_c)$. This rotation of the easy axis accompanying temperature changes is called SRT and belongs to a second-order phase transition. Critical temperatures T_L and T_H define the temperature range of SRT ($T_L < T_H$), within which the phase is described by the symbol $\Gamma_{24}(L_{ac}, M_{ac})$. These phase transitions can be found⁴⁶ in the materials RFeO_3 for $\text{R} = \text{Ho}, \text{Sm}, \text{Er}, \text{Nd}, \text{Tm}, \text{and Yb}$. At very low temperature (few Kelvins), the spins of R^{3+} are ordered due to $\text{R}^{3+}\text{--R}^{3+}$ superexchange interaction and thus make the system more complicated. Because our experiments are near room temperature, the magnetization due to R^{3+} can be ignored.

The anisotropy interaction A_{aa} is attributed to the single-ion anisotropy of Fe^{3+} , and it prefers the Γ_4 configuration. The temperature-dependent anisotropy interaction A_{cc} originates from the exchange interaction between R^{3+} and Fe^{3+} , which flavors the Γ_2 configuration. Because as the temperature decreases, the magnetic moments of the R^{3+} spins become larger, and thus enhances the $\text{Fe}^{3+}\text{--R}^{3+}$ interaction⁴⁶. When the $\text{Fe}^{3+}\text{--R}^{3+}$ interaction energy is comparable to the anisotropy energy of Fe^{3+} , the SRT occurs.

The microscopic mechanism for some examples was studied. In HoFeO_3 , ErFeO_3 and TmFeO_3 , the crystal field splits the ground state⁴⁷ of R^{3+} , where the orbital states (angular moments) of these split states are different. The magnetic moment of the R^{3+} ions is determined by the occupation of these split states^{32,48}. The thermal distribution of electrons on these split states is described by the Boltzmann factor and thus is determined by the temperature. When the temperature varies near the energy gap between the split levels, the magnetic moment of R^{3+} ions and thus the $\text{Fe}^{3+}\text{--R}^{3+}$ interaction energy changes drastically. The comparability between $\text{Fe}^{3+}\text{--R}^{3+}$ interaction energy and the

anisotropy energy of Fe^{3+} happens in this temperature range. Therefore, the SRT temperature is comparable with the energy gap between the split levels as shown in Table 2-1.

Note that, for SmFeO_3 , the crystal-field splitting has not been detected by the absorption spectrum. The possible reason is that the corresponding energy gap at 313 cm^{-1} (estimated from the SRT temperature) lies in the phonon spectrum⁴⁷. The strong absorption by phonon may cover up the absorption by the crystal-field-split levels. The energy gap (between ${}^6H_{5/2}$ and ${}^6H_{7/2}$) shown in Table 2-1 is due to the spin-orbital splitting⁴⁹. Because of the different total angular momentums J of the two states, the thermal distribution of electrons on the two states also determines the magnetic moment of the Sm^{3+} ion. By mixing different rare-earth elements such as Er and Sm, we can tune the temperature dependence of the averaging magnetic moment of the rare-earth ions and thus the SRT temperature. Because the magnetic properties are dominated by the mean-field theory where the average of the interactions between spins over a macroscopic size are considered, the local disorder induced by the different rare-earth ions around iron ions does not influence the magnetic properties and the experiment results⁴⁵.

Table 2-1| The energy gaps between split energy levels and the SRT temperatures in some rare-earth orthoferrites.

Materials	Energy gaps	SRT temperatures
TmFeO_3 [ref ^{32,47}]	$20 \text{ cm}^{-1}, 33 \text{ cm}^{-1}, 42 \text{ cm}^{-1}$	80 K – 90 K
ErFeO_3 [ref ^{47,48}]	$45 \text{ cm}^{-1}, 47 \text{ cm}^{-1}, 61 \text{ cm}^{-1}$	87 K – 97 K
HoFeO_3 [ref ^{23,47,50}]	$6 \text{ cm}^{-1}, 86.6 \text{ cm}^{-1}$	38 K – 58 K
SmFeO_3 [ref ^{45,49}]	1100 cm^{-1}	436 K – 456 K

2.3 Spin dynamics in canted antiferromagnets

In this section, we will introduce the eigenmodes of spin precessions in canted antiferromagnets and discuss the trajectories of them based on the LLG equations. Then, the LLG equations are transformed into a simpler form by using only the vector $\mathbf{L}$, which will be used in the chapters 4 and 5.

2.3.1 Derivation of eigenmodes of spin dynamics

The spin precessions are described by the LLG equations,

$$\frac{d\mathbf{m}_i}{dt} = -\gamma\mathbf{m}_i \times \mathbf{B}_{\text{eff},i} + \alpha_{\text{LLG}}\mathbf{m}_i \times \frac{d\mathbf{m}_i}{dt}, \quad (2-3)$$

$$\mathbf{B}_{\text{eff},i} = -\nabla_i V, \quad (2-4)$$

$$\begin{aligned} V = & H_E \mathbf{m}_1 \cdot \mathbf{m}_2 + H_D (m_{1c} m_{2a} - m_{1a} m_{2c}) - \mathbf{B} \cdot (\mathbf{m}_1 + \mathbf{m}_2) \\ & - A_{aa} (m_{1a}^2 + m_{2a}^2) - A_{cc} (m_{1c}^2 + m_{2c}^2) \\ & + A_4 (m_{1a}^4 + m_{1b}^4 + m_{1c}^4 + m_{2a}^4 + m_{2b}^4 + m_{2c}^4), \end{aligned} \quad (2-5)$$

where γ is the gyromagnetic ratio which approximately equals to 1.76×10^{11} rad/(S⁻¹T⁻¹), $\mathbf{B}_{\text{eff}}$ is the effective magnetic field, and α_{LLG} is the Gilbert damping parameter (with positive value). Because the phase does not influence the shape of the trajectories of the eigen modes, for simplicity, we assume that the spin system is in the phase $\Gamma_4(L_a, M_c)$.

For derivation of the eigenmodes of spin precession, the coordinates of sublattice magnetizations are transformed from the crystal coordinate system to a new system^{38,51,52},

$$\begin{pmatrix} m_{1a} \\ m_{1b} \\ m_{1c} \end{pmatrix} = \begin{pmatrix} \sin\beta_0 & 0 & \cos\beta_0 \\ 0 & 1 & 0 \\ -\cos\beta_0 & 0 & \sin\beta_0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}, \quad (2-6a)$$

$$\begin{pmatrix} m_{2a} \\ m_{2b} \\ m_{2c} \end{pmatrix} = \begin{pmatrix} \sin\beta_0 & 0 & -\cos\beta_0 \\ 0 & 1 & 0 \\ \cos\beta_0 & 0 & \sin\beta_0 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}, \quad (2-6b)$$

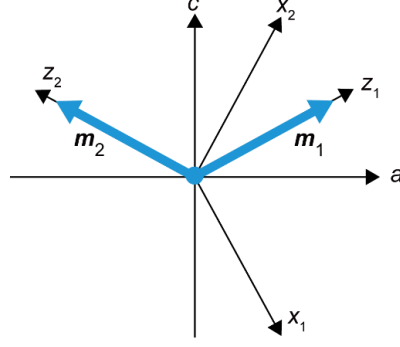


Figure 2-5. The crystal coordinate system is defined by $\{a, b, c\}$. The new frames are defined by $\{x_1, y_1, z_1\}$ and $\{x_2, y_2, z_2\}$. Note that $b \parallel y_1 \parallel y_2$.

which is visualized by Fig. 2-5. Then the LLG equations can be solved by using the new frames. The basis of eigenmodes of spin precession are introduced,

$$\sigma_z \equiv z_1 - z_2, \sigma_y \equiv y_1 + y_2, \sigma_x \equiv x_1 + x_2, \quad (2-7a)$$

$$\gamma_z \equiv z_1 + z_2 - 2, \gamma_y \equiv y_1 - y_2, \gamma_x \equiv x_1 - x_2. \quad (2-7b)$$

By using Eqs. (2-6) and (2-7) in the LLG equations, we can obtain the motion equations of two eigenmodes. Here, we ignore α_{LLG} and A_4 . α_{LLG} makes spins relax to the equilibrium and thus contributes to the perimeter of the trajectories in one cycle. Because we concern about the shape more, α_{LLG} can be ignored. A_4 is far smaller than A_{aa} and A_{cc} , and thus can be ignored.

In the perturbative regime, we can assume $z_i \approx 1 \gg x_i, y_i$. The terms of x_i and y_i in the motion equations higher than the first order are ignored. The results are introduced directly in the following where the external magnetic field $\mathbf{B}$ is assumed to be zero. The so-called q-FM mode is described by the motion equation,

$$\begin{aligned}\dot{\sigma}_x = & -\gamma(H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 \\ & + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0) \sigma_y,\end{aligned}\quad (2-8a)$$

$$\dot{\sigma}_y = 2\gamma(A_{aa} - A_{cc}) \cos 2\beta_0 \sigma_x, \quad (2-8b)$$

$$\dot{\sigma}_z = 0. \quad (2-8c)$$

The resonance frequency can be obtained by substituting Eq. (2-8b) into Eq. (2-8a),

$$\begin{aligned}\nu_{\text{FM}} = & \frac{\gamma}{2\pi} \sqrt{H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0} \\ & \times \sqrt{2(A_{aa} - A_{cc}) \cos 2\beta_0}.\end{aligned}\quad (2-9)$$

The solutions are given by,

$$\sigma_x = A_{\text{FM}} \cos (2\pi \nu_{\text{FM}} t), \quad (2-10a)$$

$$\sigma_y = A_{\text{FM}} r_{\text{FM}} \sin (2\pi \nu_{\text{FM}} t), \quad (2-10b)$$

$$\begin{aligned}r_{\text{FM}} = & \sqrt{\frac{2(A_{aa} - A_{cc}) \cos 2\beta_0}{H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0}} \\ & \sim \sqrt{\frac{A_{aa} - A_{cc}}{H_E + \beta_0 H_D + A_{aa}}} \ll 1.\end{aligned}\quad (2-10c)$$

And the q-AFM mode is described by,

$$\begin{aligned}\dot{\gamma}_x = & -\gamma(-H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 \\ & + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0) \gamma_y,\end{aligned}\quad (2-11a)$$

$$\dot{\gamma}_y = 2\gamma(H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + A_{aa} \cos 2\beta_0 - A_{cc} \cos 2\beta_0) \gamma_x, \quad (2-11b)$$

$$\dot{\gamma}_z = 0. \quad (2-11c)$$

The resonance frequency can be obtained by substituting Eq. (2-11b) into Eq. (2-11a),

$$\begin{aligned} \nu_{\text{AFM}} = & \frac{\gamma}{2\pi} \sqrt{-H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0} \\ & \times \sqrt{2(H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + A_{aa} \cos 2\beta_0 - A_{cc} \cos 2\beta_0)}. \end{aligned} \quad (2-12)$$

The solutions are given by,

$$\gamma_x = A_{\text{AFM}} \cos(2\pi \nu_{\text{AFM}} t), \quad (2-13a)$$

$$\gamma_y = A_{\text{AFM}} r_{\text{AFM}} \sin(2\pi \nu_{\text{AFM}} t), \quad (2-13b)$$

$$\begin{aligned} r_{\text{AFM}} = & \sqrt{\frac{2(H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + A_{aa} \cos 2\beta_0 - A_{cc} \cos 2\beta_0)}{(-H_E + H_E \cos 2\beta_0 + H_D \sin 2\beta_0 + 2A_{aa} \cos^2 \beta_0 + 2A_{cc} \sin^2 \beta_0)}} \\ & \sim \sqrt{\frac{2(H_E + 2\beta_0 H_D + A_{aa} - A_{cc})}{(2\beta_0 H_D + 2A_{aa})}} \gg 1. \end{aligned} \quad (2-13c)$$

2.3.2 Trajectories of spin dynamics

The traces of two eigenmodes in $\{\sigma_x, \sigma_y\}$ plane and $\{\gamma_x, \gamma_y\}$ plane are given by Eqs (2-10) and (2-13), respectively. For the rare-earth orthoferrites in our paper, the condition $A_{aa}, A_{cc} \ll H_D \ll H_E$ is known, thus we have the relation, $r_{\text{FM}} \ll 1$ and $r_{\text{AFM}} \gg 1$. Take HoFeO_3 as an example, $r_{\text{FM}} \approx 0.01$ and $r_{\text{AFM}} \approx$

60.

The orders of magnitudes of r_{FM} and r_{AFM} are not affected by the phase of spin systems. The phases include $\Gamma_2(L_c, M_a)$, $\Gamma_4(L_a, M_c)$, and $\Gamma_{24}(L_{ac}, M_{ac})$, the difference of which is the direction of $\mathbf{L}$ or $\mathbf{M}$ in a - c plane. The angle between $\mathbf{L}$ and a axis or $\mathbf{M}$ and c axis is defined by θ . In our derivation process, θ is set to zero and the system is in the phase $\Gamma_4(L_a, M_c)$. For other phases, θ is not zero. Arbitrary values of θ does not influence the first two terms in the free energy Eq (2-5) but brings the term of $\cos\theta$ or $\sin\theta$ into the last three terms. Therefore, in Eqs (2-10) and (2-13), $\cos\theta$ or $\sin\theta$ would be attached to the terms of A_{aa} and A_{cc} . This modification does not affect the relation, $r_{\text{FM}} \ll 1$ and $r_{\text{AFM}} \gg 1$.

The trajectories are visualized³⁸ in Fig. 2-6. On the one hand, we find that the q-AFM mode shows a very elliptical trajectory with the major axis along γ_y axis as shown in Fig. 2-6a. To understand this feature, we should review the basis of q-AFM mode: $\gamma_y \equiv y_1 - y_2$ and $\gamma_x \equiv x_1 - x_2$. The minus sign

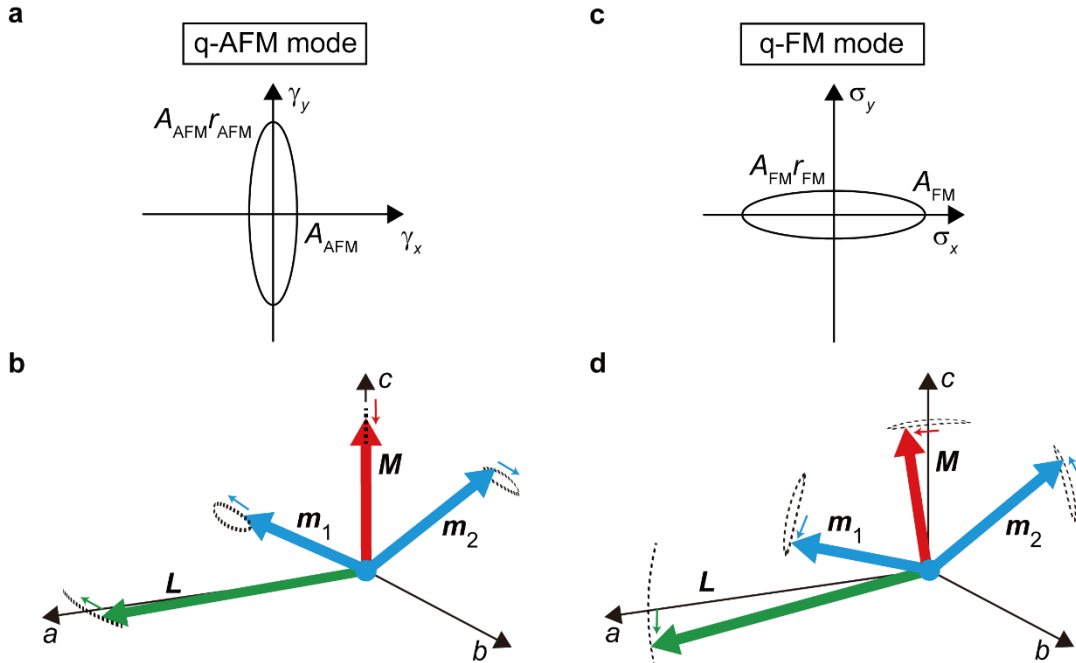


Figure 2-6. Trajectories of the q-AFM mode in $\{\gamma_x, \gamma_y\}$ plane and in the crystallographic frame $\{a, b, c\}$ are shown in **a** and **b**, respectively. Trajectories of the q-FM mode in $\{\sigma_x, \sigma_y\}$ plane and in the crystallographic frame $\{a, b, c\}$ are shown in **c** and **d**, respectively.

indicates that for q-AFM mode, $\mathbf{m}_1$ and $\mathbf{m}_2$ move to opposite directions in the corresponding frames $\{x_i, y_i, z_i\}$ ($\Delta y_1 = -\Delta y_2, \Delta x_1 = -\Delta x_2$). When viewing in the crystallography frame $\{a, b, c\}$, γ_y indicates the motion where $\mathbf{m}_1$ and $\mathbf{m}_2$ deflect to $+(-)b$ and $-(+)b$ -axis directions, respectively. γ_x indicates that $\mathbf{m}_1$ and $\mathbf{m}_2$ deflect towards $+(-)c$ -axis direction synchronously. $\gamma_y \gg \gamma_x$ means the oscillation amplitude on b axis is far larger than that on c axis. The q-AFM in the crystallographic frame is shown in Fig. 2-6b. We can find that the motion of $\mathbf{m}_i$ is an ellipse extremely compressed in the c -axis direction. Equivalently, the vector $\mathbf{M}$ oscillates in its radial direction and $\mathbf{L}$ perform a swing motion in a - b plane. q-AFM mode can be selectively excited when the THz magnetic field is parallel with $\mathbf{M}$.

On the other hand, the q-FM mode shows a very elliptical trajectory with the major axis along σ_x axis as shown in Fig. 2-6c. The basis of q-FM is given by: $\sigma_y \equiv y_1 + y_2$ and $\sigma_x \equiv x_1 + x_2$. The plus sign indicates that for q-FM the orientations of motion of $\mathbf{m}_1$ and $\mathbf{m}_2$ are same in their frames $\{x_i, y_i, z_i\}$ ($\Delta y_1 = \Delta y_2, \Delta x_1 = \Delta x_2$). When viewing in the crystallography frame, σ_y indicates the motion where $\mathbf{m}_1$ and $\mathbf{m}_2$ deflect to $+(-)b$ -axis direction synchronously. σ_x indicates that $\mathbf{m}_1$ and $\mathbf{m}_2$ deflect towards $+(-)a$ -axis direction synchronously. $\sigma_x \gg \sigma_y$ means the oscillation amplitude on a axis is far larger than that on b axis. The q-FM mode in the crystallographic frame is shown in Fig. 2-6d. It can be found that the motion of $\mathbf{m}_i$ is an ellipse extremely compressed in the b -axis direction. Equivalently, the vector $\mathbf{L}$ performs a swing motion in a - c plane, the trajectory of $\mathbf{M}$ is an ellipse which is centered at the equilibrium direction and is compressed extremely in the b -axis direction. The q-FM mode can be selectively excited by the THz magnetic field perpendicular to $\mathbf{M}$.

The results can be expanded to arbitrary phases. The spin dynamics have two eigenmodes with the very elliptical trajectories. For q-AFM mode, the ellipses of $\mathbf{m}_1$ and $\mathbf{m}_2$ are compressed in the radial direction of $\mathbf{M}$. Meanwhile, $\mathbf{M}$ oscillates in its radial direction and $\mathbf{L}$ performs a swing motion perpendicular to a - c plane. For q-FM mode, the ellipses of $\mathbf{m}_1$ and $\mathbf{m}_2$ are compressed in the direction of b axis. Besides, $\mathbf{L}$ performs a swing motion in a - c plane and $\mathbf{M}$

nearly performs a swing motion in a - c plane, but with a little b -axis component which is estimated to be 0.01 of the a - c -plane component.

2.3.3 Motion equation with respect to $\mathbf{L}$

The LLG equations are described by vectors $\mathbf{L}$ and $\mathbf{M}$ in this section. As the result of analysis, it can be found that $\mathbf{M}$ is a slave variable determined by $\mathbf{L}$ and thus the LLG equations can be described by using only $\mathbf{L}$.

By using the relations, $\mathbf{L} = (\mathbf{m}_1 - \mathbf{m}_2)/2$, $\mathbf{M} = (\mathbf{m}_1 + \mathbf{m}_2)/2$, $\mathbf{M} \cdot \mathbf{L} = 0$, and $\mathbf{M}^2 + \mathbf{L}^2 = 1$, we replace $\mathbf{m}_1$ and $\mathbf{m}_2$ with $\mathbf{M}$ and $\mathbf{L}$ in the free energy,

$$V = 2H_E \mathbf{M}^2 - 2\mathbf{M} \cdot (\mathbf{L} \times \mathbf{H}_D + \mathbf{B}) + W_a. \quad (2-14)$$

The anisotropy energy is summarized in the term W_a which includes $\mathbf{M}^2$, $\mathbf{M}^4$, $\mathbf{L}^2$ and $\mathbf{L}^4$. Because the cant angle β_0 is very small, the relation $\mathbf{M}^2 \ll \mathbf{L}^2$ is satisfied. The dependence of W_a on $\mathbf{M}$ can be ignored,

$$W_a = -2A_{aa}L_a^2 - 2A_{cc}L_c^2 + 2A_4(L_a^4 + L_b^4 + L_c^4). \quad (2-15)$$

Then we substitute $\mathbf{m}_1$ and $\mathbf{m}_2$ with $\mathbf{M}$ and $\mathbf{L}$ in the LLG equations. We can obtain the LLG equations with respect to $\mathbf{M}$ and $\mathbf{L}$,

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \frac{\partial V}{\partial \mathbf{M}} + \gamma \mathbf{L} \times \frac{\partial V}{\partial \mathbf{L}}, \quad (2-16a)$$

$$\frac{d\mathbf{L}}{dt} = \gamma \mathbf{L} \times \frac{\partial V}{\partial \mathbf{M}} + \gamma \mathbf{M} \times \frac{\partial V}{\partial \mathbf{L}}. \quad (2-16b)$$

The denominator 2 has been written in the potential V . Therefore, V is rewritten by,

$$V = H_E \mathbf{M}^2 - \mathbf{M} \cdot (\mathbf{L} \times \mathbf{H}_D + \mathbf{B}) - A_{aa} L_a^2 - A_{cc} L_c^2 + A_4 (L_a^4 + L_b^4 + L_c^4). \quad (2-17)$$

In general, for rare-earth orthoferrites, we have the relation, $A_{aa}, A_{cc} \ll |\mathbf{L} \times \mathbf{H}_D| \ll H_E$. For the equation of $d\mathbf{L}/dt$, we can obtain,

$$\mathbf{M} \times \frac{\partial V}{\partial \mathbf{L}} = -\mathbf{M} \times (\mathbf{H}_D \times \mathbf{M}) + \mathbf{M} \times \frac{\partial w_a(\mathbf{L})}{\partial \mathbf{L}}, \quad (2-18a)$$

$$\mathbf{L} \times \frac{\partial V}{\partial \mathbf{M}} = 2H_E \mathbf{L} \times \mathbf{M} - \mathbf{L} \times (\mathbf{L} \times \mathbf{H}_D + \mathbf{B}). \quad (2-18b)$$

$\mathbf{M} \times \partial V / \partial \mathbf{L}$ is on the order of $M^2 H_D$, MA_{aa} and MA_{cc} . It is much smaller than $\mathbf{L} \times \partial V / \partial \mathbf{M}$ which is on the order of MH_E and H_D . Therefore, it leads to a very important result that $\mathbf{M}$ is a slave variable which is determined by $\mathbf{L}$ and its time derivative^{23,53,54}. By solving Eq. (2-16b), $\mathbf{M}$ is given by,

$$\mathbf{M} = \frac{1}{2H_E} (\mathbf{B}_{\text{Total}} - \mathbf{L}(\mathbf{B}_{\text{Total}} \cdot \mathbf{L}) + \frac{\dot{\mathbf{L}} \times \mathbf{L}}{\gamma}), \quad (2-19)$$

where $\mathbf{B}_{\text{Total}} = \mathbf{L} \times \mathbf{H}_D + \mathbf{B}$. Then, by inserting Eq. (2-19) into Eq. (2-16a), we can obtain the equation of motion with respect to $\mathbf{L}$,

$$\begin{aligned} & \dot{\mathbf{L}} \times \mathbf{H}_D + \dot{\mathbf{B}} - \dot{\mathbf{L}}(\mathbf{B} \cdot \mathbf{L}) - \mathbf{L}(\dot{\mathbf{B}} \cdot \mathbf{L} + \mathbf{B} \cdot \dot{\mathbf{L}}) + \frac{\ddot{\mathbf{L}} \times \mathbf{L}}{\gamma} = \\ & -\gamma(\mathbf{L} \times \mathbf{H}_D) \times \mathbf{B} + \gamma(\mathbf{B} \cdot \mathbf{L})\mathbf{L} \times \mathbf{B} - (\dot{\mathbf{L}} \times \mathbf{L}) \times \mathbf{B} \\ & + 2H_E \gamma \mathbf{L} \times \frac{\partial V}{\partial \mathbf{L}}. \end{aligned} \quad (2-20)$$

According to the discussion about the trajectories of the q-AFM and the q-FM modes, Eq. (2-20) can be decomposed into two motion equations for two

eigenmodes. The b -axis component of the equation corresponds to the q-FM mode, because $\mathbf{L}$ shows the swing motion in a - c plane leading to $\ddot{\mathbf{L}} \times \mathbf{L}$ oriented at b axis. Besides, the q-AFM mode is described by the a -axis and c -axis components due to the swing motion of $\mathbf{L}$ perpendicular to a - c plane.

2.4 Magneto-optic effect

The spin dynamics are probed based on the Magneto-optic effect by measuring the variation of the polarization states of probe pulses transmitting through the sample. The Magneto-optic effect is introduced here starting with the simplest case (a paramagnet). The dielectric tensor of an isotropic material is given by⁵⁵,

$$\begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{xx} \end{pmatrix}. \quad (2-21)$$

A magnetic field is applied along z axis to magnetize the sample, and a probe light propagating along z axis (laboratory coordinate) is incident into x - y plane of the sample. The symmetry of the sample is lowered by the magnetization M , and the dielectric tensor is given by,

$$\begin{pmatrix} \epsilon_{xx}(M) & \epsilon_{xy}(M) & 0 \\ -\epsilon_{xy}(M) & \epsilon_{xx}(M) & 0 \\ 0 & 0 & \epsilon_{zz}(M) \end{pmatrix}. \quad (2-22)$$

Then based on the Onsager principle, $\epsilon_{ij}(-M) = \epsilon_{ji}(M)$, the diagonal and off-diagonal elements can be expanded as the sum of even-order terms and odd-order terms of M , respectively. In general, the off-diagonal elements contribute to Faraday effect and Kerr effect, while the diagonal elements lead to Cotton-mouton effect.

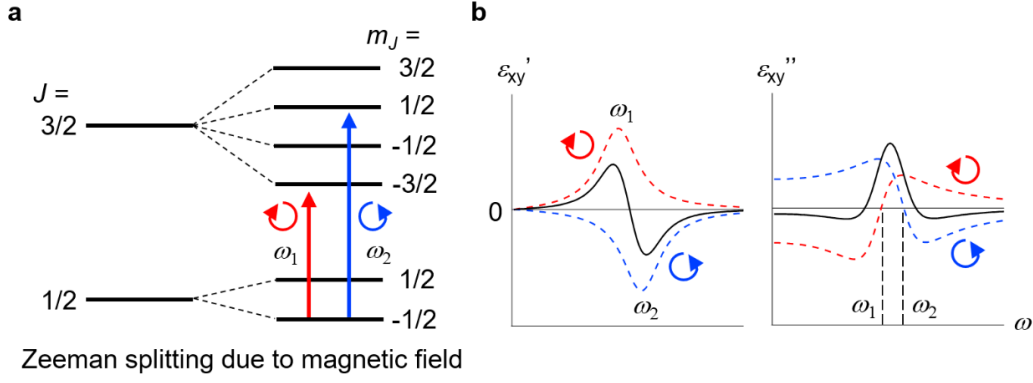


Figure 2-7. Schematic of the microscopic mechanism of magneto-optic effect. **a**, A two-level system with the ground state (total angular momentum $J = 1/2$) and the excited state ($J = 3/2$). **b**, The dispersion of ϵ_{xy} . ϵ_{xy}' and ϵ_{xy}'' are the real and imaginary parts, respectively. Black curves are the summation of the red and blue curves.

Based on the quantum mechanics, the detail form of ϵ_{xy} can be obtained,

$$\epsilon_{xy} = \frac{Nq^2}{2i\epsilon_0\hbar} \sum_j \omega_{j0} \frac{|\langle 0|x^+|j\rangle|^2 - |\langle 0|x^-|j\rangle|^2}{\omega_{j0}^2 - (\omega + i\gamma)^2}, \quad (2-23)$$

where N and q are the density and the charge of the electric dipole, respectively. $|\langle 0|x^+|j\rangle|^2$ and $|\langle 0|x^-|j\rangle|^2$ indicate the transition possibilities from ground state $|0\rangle$ to excited state $|j\rangle$ when a left and a right circularly polarized photons are absorbed, respectively. If the application of magnetic field largely splits the energy levels of the spin-orbit-coupled states, ϵ_{xy} becomes large. For example, there is a system with spin-orbit coupling as shown in Fig. 2-7a. The ground state and the excited state have total angular momenta $J = 1/2$ and $3/2$, respectively. The application of magnetic field lifts the degeneracy of the states, due to Zeeman splitting. We focus on one ground state with $m_J = -1/2$. The transitions to the excited states with $m_J = -3/2$ and $1/2$ are allowed by the selective rule. The transitions of $m_J = -1/2 \rightarrow -3/2$ and $-1/2 \rightarrow 1/2$ can be excited by a left and right circularly polarized photon, respectively. Because the two transitions have different energy gaps, the dispersion curves ϵ_{xy} for left and right circularly polarized photon are shifted as shown in Fig. 2-7b, thus

leading to a nonzero dispersion for the summation which is given by Eq. (2-23).

For the case of rare-earth orthoferrites, the material is not isotropic, but has large birefringence, which is even stronger than the magneto-optic effect. Besides, the magnetic order of antiferromagnet is described by two parameters, $\mathbf{m}_1$ and $\mathbf{m}_2$, or $\mathbf{L}$ and $\mathbf{M}$, so the dielectric tensor elements are expanded to the terms combining $\mathbf{L}$ and $\mathbf{M}$, such as⁵⁶,

$$\begin{aligned}\varepsilon_{ij} = \varepsilon_{ij}^{(0)} + if_{ijk}M_k + ig_{ijk}L_k \\ + a_{ijkl}M_kM_l + b_{ijkl}L_kL_l + c_{ijkl}M_kL_l.\end{aligned}\quad (2-24)$$

In general, to explain the magneto-optic effect for probe light at 800 nm in rare-earth orthoferrites, expanding to the first-order term is enough (the second-order term related to Cotton-mouton effect is small.)⁵⁶⁻⁵⁹. In our experiment setup, we have the relations $x//a$, $y//b$ and $z//c$.

Therefore, the dielectric tensor in x - y plane is given by,

$$\begin{pmatrix} \varepsilon + \sigma & i\kappa \\ -i\kappa & \varepsilon - \sigma \end{pmatrix}, \quad (2-25)$$

$$\kappa = f \cdot \frac{M_0 + \Delta M_c}{M_0} + g \cdot \frac{L_0 + \Delta L_a}{L_0}, \quad (2-26)$$

where, σ represents the birefringence independent of the magnetic order. The equilibrium values of $\mathbf{M}$ and $\mathbf{L}$ are given by M_0 and L_0 . The strengths of magnetic birefringence contributed by $\mathbf{M}$ and $\mathbf{L}$ are defined by using phenomenological parameters f and g , respectively. As the probe pulses transmit through the sample, the polarization states are varied by nonzero ΔM_c and ΔL_a . For example, before incidence, probe pulses are linearly polarized along $b(y)$ axis. When leaving the sample, probe pulses become ellipses with

the ellipticity angles η . The angle between major axis of the ellipse and $b(y)$ axis is defined by ϕ .

Chapter 3 Experiment setup

The coherent spin dynamics in our experiments are investigated by the time-resolved pump-probe measurement. The beam of laser pulses at 800 nm generated from the source are divided into a pump beam and a probe beam. The pump pulses are used to generate the strong THz pulses in the electro-optic crystal LiNbO_3 based on the tilted-optical-pulse-front method. The Tesla-class THz magnetic near fields are generated by irradiating the microresonators on the sample surface with the strong THz pulses. A microresonator is composed of an antenna part and a solenoid part, where the THz pulses are coupled to the microresonator via the antenna part to generate THz currents and the near fields are induced in the solenoid part. The magnetic near fields excite the coherent spin dynamics in the samples. For detection of the coherent spin dynamics, the probe pulses are incident into the sample. The polarization states of probe pulses are modified by the spin dynamics and are detected by an analyzer. By varying the time difference between pump and probe pulses arriving the sample, the spin dynamics can be detected in the time domain.

3.1 THz generation and detection

THz radiation is electromagnetic radiation at frequencies between the infrared and microwave region, that is $10^{11} \sim 10^{13}$ Hz. This region covers lots of resonances of intriguing physical processes such as rotations of molecules, lattice vibrations (phonons) in solids, exciton intraband transitions in semiconductors, and BCS gaps in superconductors. In order to study these processes, the technologies to generate and detect THz wave are developed explosively in the last three decades.

THz sources are classified into continuous-wave (CW) and broad-band-pulse generation, and THz detectors also have two types, incoherent and coherent detection. The incoherent techniques are similar with Fourier transform

infrared spectroscopy (FTIR) which only measures the intensity, but the coherent techniques simultaneously detect the amplitude and phase of THz wave. In this chapter, we introduce the technique about THz-pulse generation and coherent detection using electro-optic (EO) crystal^{60–63}.

3.1.1 THz generation using optical nonlinear crystal

There are lots of THz-pulse sources, such as photoconductive antenna, electron accelerator, optical nonlinear crystal, and air plasma. It has been demonstrated that LiNbO₃ crystal as an optical nonlinear crystal enables the generation of intense single-cycle THz pulses with peak amplitude about 1 MV/cm and a broad-band spectrum centered around 1 THz⁶⁴, which can be used to excite the spin precession efficiently. In this section, we will explain the method of THz generation with LiNbO₃ crystal.

THz generation by impinging ultrafast optical pulses into nonlinear crystal is one of the second-order optical process, called optical rectification^{63,65}. This process induces the nonlinear polarization given by,

$$P_i^{(2)}(\omega_{\text{THz}}) = \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)}(\omega_{\text{THz}}; \omega_o + \omega_{\text{THz}}, -\omega_o) \times \int_{-\infty}^{\infty} E_j(\omega_o + \omega_{\text{THz}}) E_k^*(\omega_o) d\omega_o, \quad (3-1)$$

$$P_i^{(2)}(t) = \int_{-\infty}^{\infty} P_i^{(2)}(\omega_{\text{THz}}) e^{-i\omega_{\text{THz}}t} d\omega_{\text{THz}}, \quad (3-2)$$

where ω_o and ω_{THz} are the frequencies of optical and THz pulses, respectively. The THz electric field is emitted by the acceleration of the polarization (the second derivative with respect to time),

$$E_{\text{THz},i} \propto \frac{d^2 P_i^{(2)}(t)}{dt^2}. \quad (3-3)$$

From these equations, we found that the nonlinear susceptibilities $\chi_{ijk}^{(2)}$ are important for THz generation. Besides, the phase matching condition is also necessary, which means that the phase velocity of THz pulse should be same as the group velocity of optical pulse. When it is satisfied, the THz pulse generated at each point in the past would constructively interfere during the propagation of probe pulse through the crystal. To evaluate the extent of the matching between the phase velocity of THz pulse and the group velocity of optical pulse, the coherence length l_c is used. l_c is defined by,

$$l_c(\omega_{\text{THz}}) = \frac{\pi c}{\omega_{\text{THz}} |n_g - n_{\text{THz}}|}, \quad (3-4)$$

where n_g is the group index of optical pulse, and n_{THz} is the refractive index of THz pulse at ω_{THz} . When 800-nm pulse is used, ZnTe ($l_c(2\text{THz}) > 3\text{ mm}$) crystal is one of the most typical crystal for THz generation⁶⁶. However, it is difficult to generate strong THz pulses using ZnTe. The bandgap of ZnTe is 2.37 eV (523 nm), so when the pump power is increased, the two-photon absorption happens, leading to the carrier generation. The carriers absorb THz fields and thus limit the efficiency of THz generation.

The crystal LiNbO₃ has a large bandgap (4.5 eV) and a large nonlinear susceptibility (2.5 times of that of ZnTe), and thus is thought to be a potential

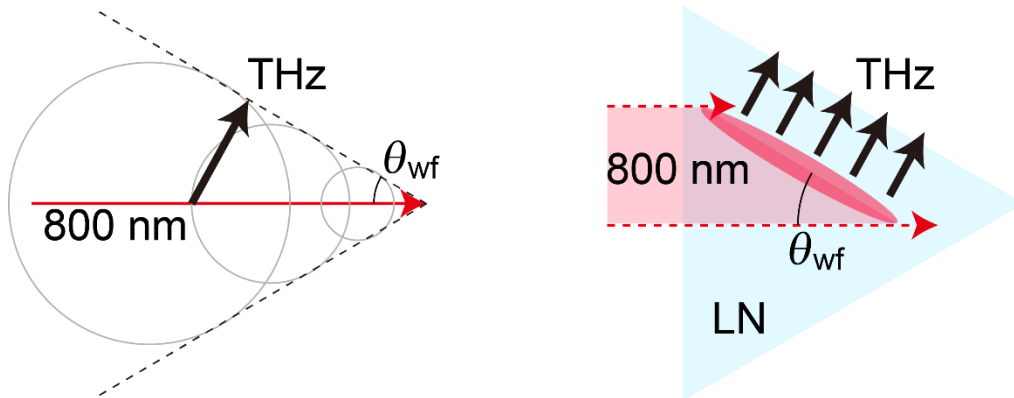


Figure 3-1. Left panel: The emission of THz pulses generated by the optical pulses propagating in the EO crystal; Right panel: THz emission by optical pulses with tilted intensity front under the condition of phase matching (LN is short for LiNbO₃).

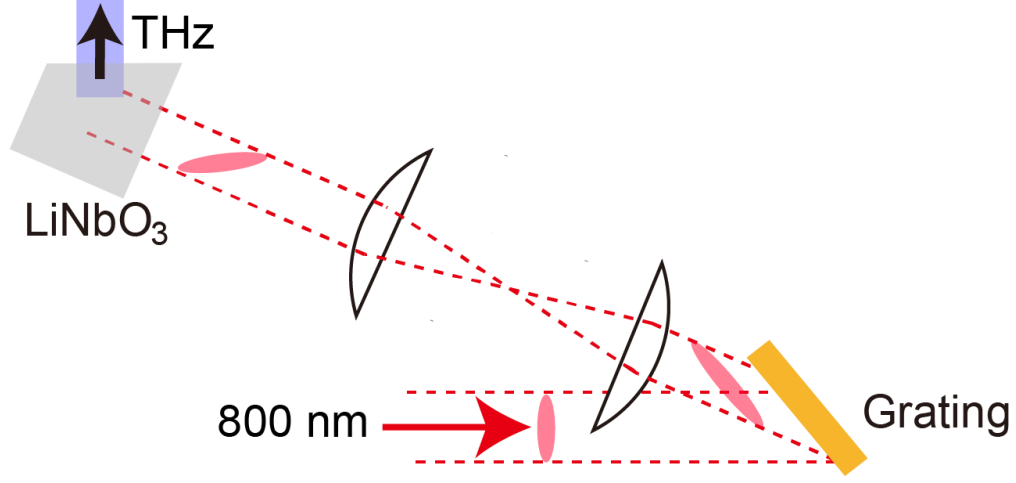


Figure 3-2. Tilted intensity front created by a grating and a pair of cylindrical lenses.

candidate for strong THz generation. However, because n_g at 800 nm is 2.23 but n_{THz} is 5.16, LiNbO₃ has a very short coherence length, thus limiting the generation efficiency. A decade ago, to overcome this shortage, a technique using tilted-optical-pulse front is put forward by Hebling et al.^{67,68}. Because of $n_{\text{THz}} > n_g$, the optical pulse in LiNbO₃ crystal propagates faster than the spread of the phase of THz wave as shown in Fig. 3-1. The propagation of THz wavefront forms a cone with a cone half angle θ_{wf} ,

$$\sin\theta_{\text{wf}} = \frac{v_{\text{THz}}}{v_g} = \frac{n_g}{n_{\text{THz}}}. \quad (3-5)$$

Hebling et al. developed the theory: If the intensity front of the optical pulse was tilted to form angle θ_{wf} with respect to the propagating direction, the effective group velocity of intensity front of optical pulse would be coincident with the phase velocity of THz pulse, so that the THz pulses can be effectively emitted. For LiNbO₃ crystal, θ_{wf} is approximately 30 degrees. The tilted intensity front can be created by a grating and a pair of cylindrical lenses⁶⁴ as shown in Fig. 3-2.

3.1.2 THz detection using electro-optic sampling

In this section, we will present the coherent detection method of the THz pulses. The 800 nm pulses with a pulse duration of 80 fs and a pulse energy of 7 mJ are generated from an amplified Ti:sapphire laser with a repetition rate of 1kHz. The output beam is divided into two beam paths by using a beam sampler of which the power ratio is 99:1. The strong one (pump beam) is employed to generate THz pulses as discussed in the last subsection, and the weak one (probe beam) is exploited for THz detection. The mechanism of THz detection using EO crystal (EO sampling) is the Pockels effect, which is the reverse process of optical rectification. Due to Pockels effect, the polarization in EO crystal induced by optical probe pulses and THz pump pulses is given by,

$$P_i^{(2)}(\omega_o) = \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)}(\omega_o; \omega_o, 0) E_j(\omega_o) E_k^*(0), \quad (3-6)$$

where the THz electric field here is regarded as a static field for simplicity. This equation indicates that the static electric field induces birefringence at optical frequencies in EO crystal. When the linearly polarized optical pulse with femtosecond duration transmits through the crystal together with the THz pulse which has a much longer duration, the birefringence induced by THz field will

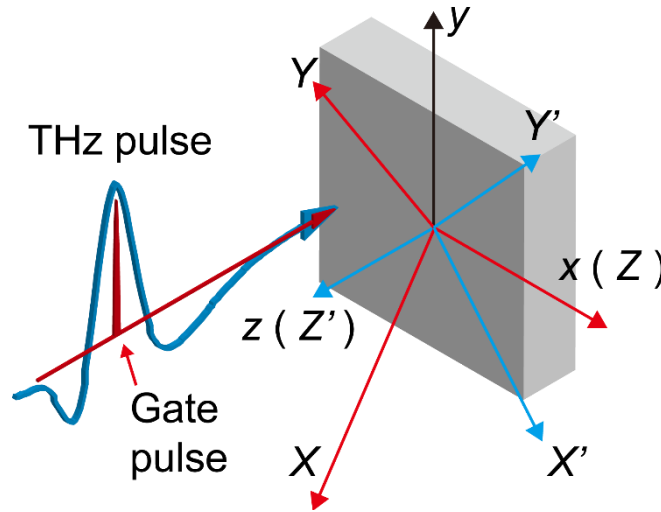


Figure 3-3. Definition of various coordinates. $\{x, y, z\}$ is the laboratory coordinate; $\{X, Y, Z\}$ is the principal axis of (110) zincblende crystal without THz electric field; $\{X', Y', Z'\}$ is the new principal axis induced by THz electric field.

modify the polarization state of optical probe pulse. The optical pulse here is also called the gate pulse, and the method to detect the THz electric field by measuring the ellipticity of the gate pulse is called EO sampling. Same as the THz generation, for efficient detection, long coherence length is required, thus the EO crystals such as ZnTe and GaP are suitable. The two crystals have the zincblende structure, and the index ellipsoid when applied by electric field $\mathbf{E}$ is described as,

$$\frac{X^2}{n_0^2} + \frac{Y^2}{n_0^2} + \frac{Z^2}{n_0^2} + 2r_{41}(E_XYZ + E_YZX + E_ZXY) = 1, \quad (3-7)$$

where r_{41} is the electro-optic coefficient, and $\{X, Y, Z\}$ is the coordinate system of the principle axis of the EO crystal. When the THz pulse polarized along $[\bar{1}, 1, 0]$ is normally incident into the (110) plane as shown in Fig. 3-3, i.e., $\mathbf{E}_{\text{THz}} = (-E_{\text{THz}}/\sqrt{2}, E_{\text{THz}}/\sqrt{2}, 0)$, the index ellipsoid becomes,

$$\frac{X^2}{n_0^2} + \frac{Y^2}{n_0^2} + \frac{Z^2}{n_0^2} + \sqrt{2}r_{41}(-E_{\text{THz}}YZ + E_{\text{THz}}ZX) = 1, \quad (3-8)$$

$$(X \ Y \ Z) \begin{pmatrix} \frac{1}{n_0^2} & 0 & \frac{\sqrt{2}r_{41}E_{\text{THz}}}{2} \\ 0 & \frac{1}{n_0^2} & -\frac{\sqrt{2}r_{41}E_{\text{THz}}}{2} \\ \frac{\sqrt{2}r_{41}E_{\text{THz}}}{2} & -\frac{\sqrt{2}r_{41}E_{\text{THz}}}{2} & \frac{1}{n_0^2} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = 1. \quad (3-9)$$

The coordinate system based on the principal axis is transformed into the system based on the new principal axis created by the THz electric field. All coordinate systems are shown in Fig. 3-3. The index ellipsoid in the new principal axis is given by,

$$(X' \quad Y' \quad Z') \begin{pmatrix} \frac{1}{n_0^2} + r_{41} E_{\text{THz}} & 0 & 0 \\ 0 & \frac{1}{n_0^2} - r_{41} E_{\text{THz}} & 0 \\ 0 & 0 & \frac{1}{n_0^2} \end{pmatrix} \begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = 1. \quad (3-10)$$

The new principal axis can be obtained by rotating from the old one,

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{\sqrt{2}} \\ -\frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} \\ \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}. \quad (3-11)$$

The THz electric field in the new axis becomes,

$$\begin{pmatrix} \frac{-E_{\text{THz}}}{\sqrt{2}} \\ \frac{E_{\text{THz}}}{\sqrt{2}} \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{\sqrt{2}} \\ -\frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} \\ \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \end{pmatrix} \begin{pmatrix} \frac{-E_{\text{THz}}}{\sqrt{2}} \\ \frac{E_{\text{THz}}}{\sqrt{2}} \\ 0 \end{pmatrix}. \quad (3-12)$$

It means that the angle between new principal axis and THz electric field is 45° . By assuming $r_{41} E_{\text{THz}} \ll 1/n_0^2$, the refractive index in the new principal axis is given by,

$$n_{X'} \approx n_0 - \frac{r_{41} n_0^3 E_{\text{THz}}}{2}, \quad (3-13a)$$

$$n_{Y'} \approx n_0 + \frac{r_{41} n_0^3 E_{\text{THz}}}{2}. \quad (3-13b)$$

Under the condition where the gate pulse is coaxially incident and is polarized parallel with the THz electric field, the components in X' and Y' axes of the gate pulse propagating in the EO crystal exhibit a phase retard. When the EO crystal has the thickness l , the phase retard of the gate pulse leaving the sample is given by,

$$\Gamma = \frac{\omega_0 l}{c} (n_{Y'} - n_{X'}) = \frac{2\pi E_{\text{THz}}}{\lambda} l r_{41} n_0^3, \quad (3-14)$$

where λ is the wavelength of the probe pulse. Hereafter, all vectors are written using the laboratory coordinate $\{x, y, z\}$. Before incidence, the polarization of the gate pulse is given by $\mathbf{E}_0 = (0, E_{\text{gate}})$. After EO sampling, it becomes,

$$\begin{aligned} \mathbf{E}_1 &= E_{\text{gate}} \begin{pmatrix} \cos \frac{\pi}{4} & \sin \frac{\pi}{4} \\ -\sin \frac{\pi}{4} & \cos \frac{\pi}{4} \end{pmatrix} \begin{pmatrix} e^{\frac{i\Gamma}{2}} & 0 \\ 0 & e^{-\frac{i\Gamma}{2}} \end{pmatrix} \begin{pmatrix} \cos \frac{\pi}{4} & -\sin \frac{\pi}{4} \\ \sin \frac{\pi}{4} & \cos \frac{\pi}{4} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= E_{\text{gate}} \begin{pmatrix} i \sin \frac{\Gamma}{2} \\ \cos \frac{\Gamma}{2} \end{pmatrix}. \end{aligned} \quad (3-15)$$

If the intensities of the x -axis and y -axis components of the gate pulse were decomposed and detected by the balanced detector directly, the relation between the signal and the THz electric field would obey the function, $(I_y - I_x)/(I_y + I_x) = \cos \Gamma = \cos (2\pi E_{\text{THz}} l r_{41} n_0^3 / \lambda)$, where I_y and I_x are the intensities of the y -axis and x -axis components, respectively. Because cosine function is even, the sign of electric field cannot be obtained. In our experiment, the THz electric field is detected by using a set of quarter wave plate, Wollaston prism and a balance detector as shown in Fig. 3-4. The polarization of the gate pulse passing the quarter wave plate is given by,

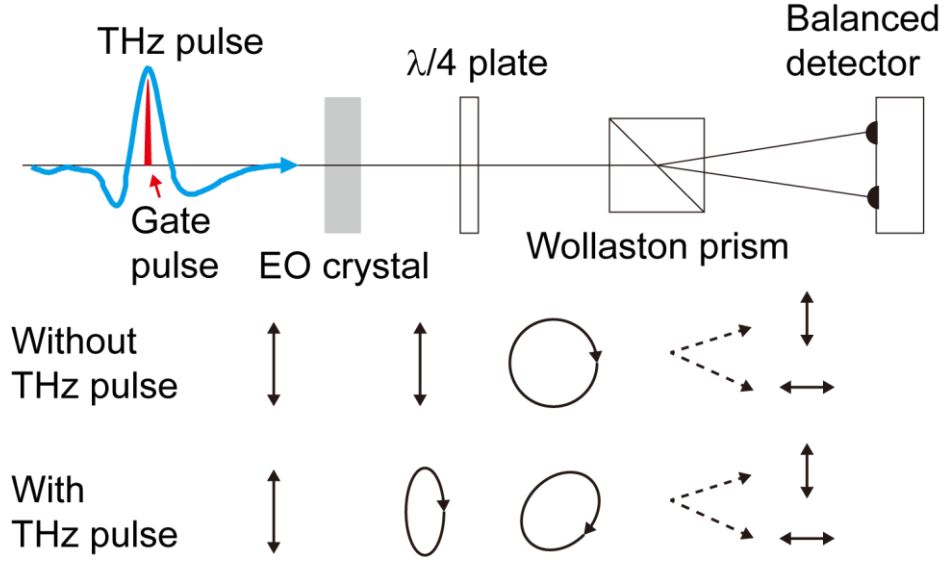


Figure 3-4. Upper panel: Schematic of THz detection; Lower panel: Polarization state of probe pulse before or after each optics.

$$\begin{aligned}
 \mathbf{E}_2 &= \begin{pmatrix} \cos \frac{\pi}{4} & \sin \frac{\pi}{4} \\ -\sin \frac{\pi}{4} & \cos \frac{\pi}{4} \end{pmatrix} \begin{pmatrix} e^{i\frac{\pi}{4}} & 0 \\ 0 & e^{-i\frac{\pi}{4}} \end{pmatrix} \begin{pmatrix} \cos \frac{\pi}{4} & -\sin \frac{\pi}{4} \\ \sin \frac{\pi}{4} & \cos \frac{\pi}{4} \end{pmatrix} \mathbf{E}_1 \\
 &= E_{\text{gate}} \begin{pmatrix} i(\sin \frac{\Gamma}{2} + \cos \frac{\Gamma}{2}) \\ \cos \frac{\Gamma}{2} - \sin \frac{\Gamma}{2} \end{pmatrix}.
 \end{aligned} \tag{3-16}$$

After the Wollaston prism, the gate pulse is decomposed into the x-axis and y-axis components and the intensities of the two components are detected by the balanced detector. The signal is given by,

$$\frac{I_x - I_y}{I_x + I_y} = \sin \Gamma = \sin \left(\frac{2\pi E_{\text{THz}}}{\lambda} l r_{41} n_0^3 \right). \tag{3-17}$$

Therefore, we can obtain the THz electric field E_{THz} from the detected quantity $(I_x - I_y)/(I_x + I_y)$. Furthermore, the time delay t between THz pulse and probe pulse is varied slowly by a delay stage, thus a temporal waveform of THz

field can be reproduced by detecting the value of E_{THz} at each time delay t . The time resolution is limited by the pulse duration of the probe pulse.

3.2 THz resonator

In this section, the THz resonators are introduced. An individual THz resonator is similar as a LC (inductance-capacitance) circuit with micrometer size. When a resonator is irradiated by THz electromagnetic wave, the LC oscillation can be excited and THz current flows in the resonator. As a result, the electric and magnetic near fields which are far stronger compared with the THz far field can be generated. The typical resonator is the split-ring resonator. In the subsection 3.2.2, Our studies using the electric near field is briefly introduced. Besides, the magnetic near field has been used to study spin dynamics in the other works. However, because the magnetic near fields generated by the split-ring resonators are not strong enough, the studies are limited to a restricted range of phenomena. Therefore, we designed a new resonator called spiral-shaped antenna resonator to generate stronger magnetic near fields. The spiral-shaped antenna resonator is used for the studies of nonlinear spin dynamics in the chapters 4 and 5.

3.2.1 Split-ring resonator

A single split-ring resonator (SRR) is shown in Fig. 3-5. When the incident THz electric field is parallel with the gap, the circularly oscillating current is

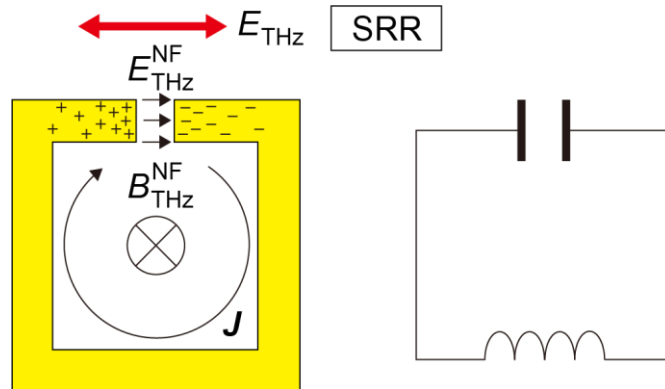


Figure 3-5. Left panel: a split-ring resonator; Right panel: a LC circuit.

generated due to LC oscillation^{69–71}. The frequency of LC oscillation covers the range from optical wave to microwave and is mainly determined by the size scale of a single element which can be tuned from hundreds of nanometers to few millimeters. In the gap which is like a capacitance, the circular current accumulates a lot of charges and thus generates a strong electric field. The strong electric field has been exploited for the excitation of nonlinear phenomena^{72–74} such as THz-field-induced insulator-to-metal transition.

3.2.2 Vacuum Rabi splitting realized with split-ring resonator

In addition, because the gap can also confine the THz vacuum fluctuation (vacuum field or vacuum photon⁷⁵) in a very small volume beyond the diffraction limit, the THz vacuum fluctuation in the gap becomes very strong⁷⁶. Therefore, the SRR is also broadly used as a cavity in the studies of vacuum Rabi splitting^{77–79}. The term “vacuum” indicates that even without the external AC electric field, the Rabi splitting can happen due to the coupling between the material and the cavity via vacuum fluctuation.

For example, as a two-level atom at the excited state is put in a cavity shown in Fig. 3-6a, due to the perturbation of vacuum fluctuation, the spontaneous emission of a photon happens^{80,81}. If the photon frequency was same as the frequency of a cavity mode, the photon would be reflected by the mirror of the cavity and then is reabsorbed by the atom. If there was no loss of photons, the process would repeat forever: emission→absorption→emission... As a result, the states of cavity and atom are hybridized to generate new eigenstates, polaritons. Compared to the energy levels of the cavity or atom, the energy levels of the polaritons exhibit a splitting as shown in Fig. 3-6b, where the splitting is defined by Ω_R . The splitting is called vacuum Rabi splitting. When the loss rates of the photon in the cavity and atom are nonzero but are smaller than the bounce rate between the cavity and atom, vacuum Rabi splitting also occurs. The two-level atom can be replaced by an arbitrary two-level system.

The coupling strength between the two-level system and the cavity is

evaluated by $\varsigma = \Omega_R/(2\omega_c)$, where the splitting frequency Ω_R is proportional to the field strength of the vacuum fluctuation. To obtain stronger coupling, stronger vacuum fluctuation is required. Therefore, SRR should be used. For the example shown in Fig. 3-6c, we fabricated SRRs on the quartz substrate and then the substrate is coated by a thin film of perovskite semiconductor MAPbI₃. The phonons at 0.95 THz in MAPbI₃ are coupled to the LC mode of SRRs (cavity mode). By varying the size L of the SRRs, we can tune the cavity frequency. As the cavity frequency approaches the phonon frequency, the polaritons appear and their frequencies exhibit a voided crossing which can be well reproduced by the theoretical results using the Hopfield model. The behavior indicates the presence of vacuum Rabi splitting. Based on the results with different gap size G , we can conclude that the smaller gap induces the stronger THz vacuum fluctuation, thus leading to the larger vacuum Rabi splitting. For $G = 0.1 \mu\text{m}$, we can obtain $\varsigma = 0.24$, which indicates that our

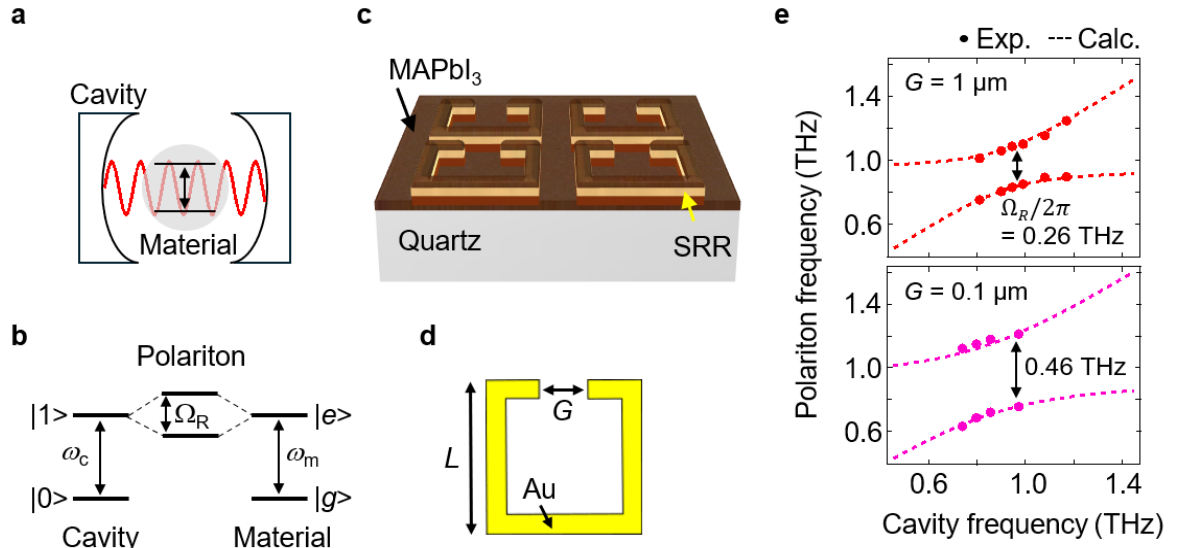


Figure 3-6. **a**, Schematic of a two-level system (atom or material) in a cavity. The red curve refers to the photon which jumps between the two-level system and the cavity. **b**, Schematic of vacuum Rabi splitting. **c**, SRRs are fabricated on a quartz substrate, and the substrate is coated by a thin film of perovskite semiconductor MAPbI₃. Phonons in MAPbI₃ are coupled to the LC mode of SRRs via vacuum THz fluctuation. **d**, Dimensions of a single SRR. **e**, The polariton dispersions for $G = 1 \mu\text{m}$ and $0.1 \mu\text{m}$. Figure reprinted with permission from the reference ⁷⁹, © 2021 American Physical Society under the terms of the Creative Commons Attribution 4.0 International license.

system reaches the ultrastrong coupling regime. The ultrastrong coupling regime is predicted to be important for the manipulation of quantum properties of the material, the quantum information procession and the vacuum-boost nonlinear optics⁸².

3.2.3 Excitation of spin dynamics with split-ring resonator

On the other hand, the ring of SRR is similar as an inductance, the circular current generates a strong magnetic field perpendicular to the sample plane. The magnetic near field is demonstrated by Kumar et. al. for the first time⁸³. They fabricated the SRR on the surface of a paramagnetic crystal TGG (terbium gallium garnet) and detected the distribution of the magnetic near field based on Faraday effect. Then, researchers managed to employ the magnetic near field exciting THz spin dynamics in antiferromagnets^{84–86}.

In the work⁸⁵, the q-FM mode was studied using the magnetic near field. The vector $\mathbf{M}$ was set perpendicular to magnetic near field, so that only q-FM mode can be excited, as shown in Fig. 3-7a. The size of SRR was adjusted so that the q-FM mode can be excited resonantly. The probe pulses were focused at the center of the ring of SRR to detect the spin dynamics. The temporal developments and the spectra of the q-FM mode were observed as shown in Figs. 3-7b and c, respectively. However, the nonlinearities were not found.

Then, Mukai et. al. improved the experiment⁸⁶. Because the magnetic near field is strongest near the corner as shown in Fig. 3-7d, they probed the spin dynamics at the corner by focusing the probe pulse via an objective lens. In that work, q-AFM mode was studied. The temporal development of the q-AFM mode is shown in Fig. 3-7e. The spectra of q-AFM mode at different field strengths are shown in Fig. 3-7f. They found that the q-AFM mode exhibits a frequency redshift but did not explain the origin of the red shift. Aside from this, they also have not observed the remarkable nonlinearities.

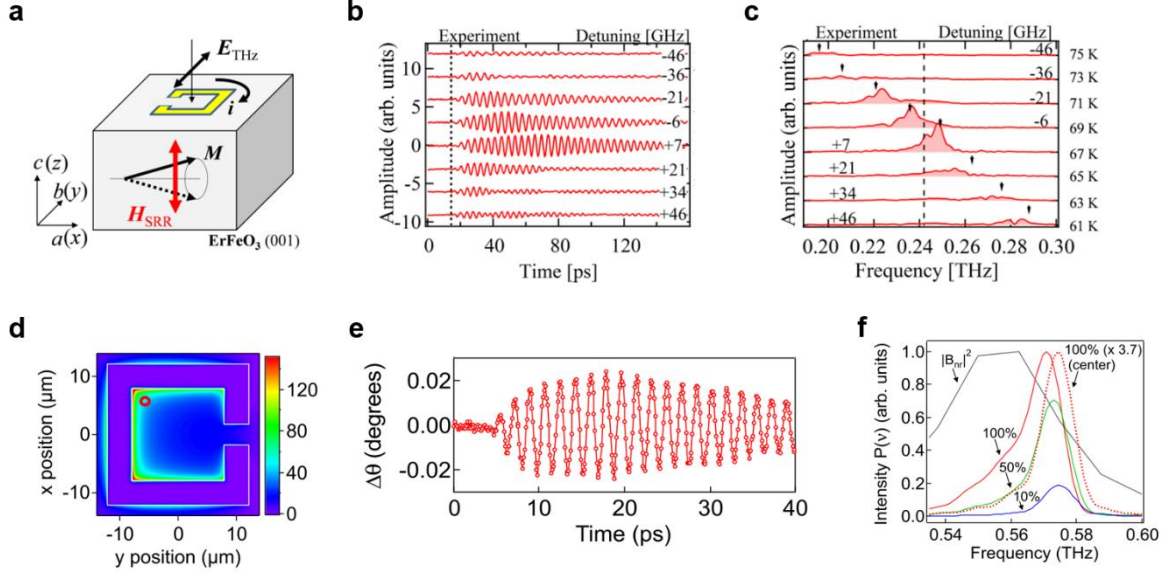


Figure 3-7. **a**, The magnetic near fields generated by a SRR on the surface of ErFeO_3 excite the q-FM mode. **b**, The temporal developments of q-FM mode at different temperatures. **c**, The temperature dependence of the spectra of the q-FM mode. Figure reprinted with permission from the reference⁸⁵, © 2014 American Physical Society. **d**, The distribution of the enhancement factor. **e**, The temporal development of the q-AFM mode. **f**, The spectra of q-AFM under different field strengths. Figure reprinted with permission from the reference⁸⁶, © 2016 IOP Publishing under the terms of the Creative Commons Attribution 3.0 licence.

3.2.4 Spiral-shaped antenna resonator

For the investigation of the spin nonlinearities, stronger excitation is required. Here, we develop a structure called spiral-shaped antenna resonator (SAR) as shown in Fig. 3-8 which consists of a long arm and a solenoid^{87–92}. The long arm is analogy as a THz antenna, and thus the parallel THz electric fields, which impinge the sample surface perpendicularly, can be coupled to the resonator via the arm. The THz electric fields drive eddy currents into the solenoid. Thus, the magnetic near fields perpendicular to the surface are generated at the center of the solenoid. Compared to SRR where the eddy currents flow in a ring with a diameter about 20 μm , SAR has a much smaller ring (solenoid) with a diameter about 4 μm . The magnetic near fields are confined inside the small hot spot and thus are much stronger. The SAR as a

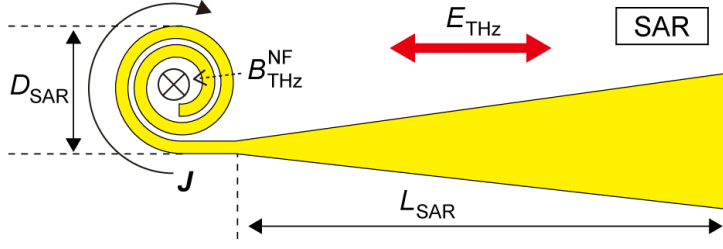


Figure 3-8. Schematic of a spiral-shaped antenna resonator.

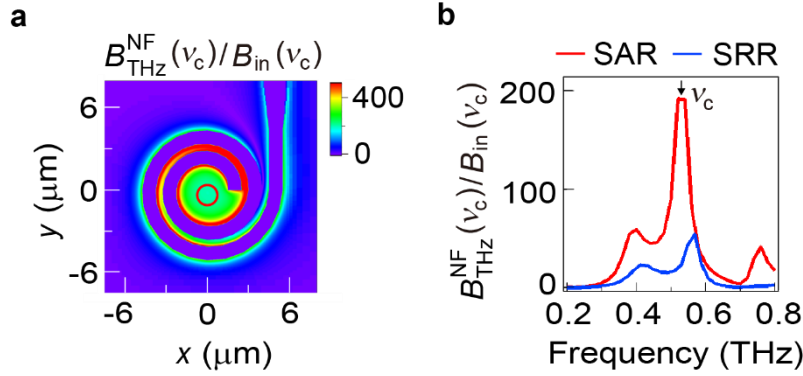


Figure 3-9. **a.** Distribution of the enhancement factor. B_{THz}^{NF} and B_{in} are the THz magnetic near field in the sample and the THz magnetic far field before incidence. **b.** Spectra of enhancement factor. The red curve is the enhancement factor at the center of the solenoid of SAR which is highlighted by the red circle in **a**. The blue curve is the enhancement factor at the corner of SRR which is indicated by the red circle in Fig.3-7d. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

whole is also similar as a LC circuit. The eddy currents oscillate in the resonator, and the resonant frequency can be described by the expression, $\nu_c = 1/(2\pi\sqrt{LC})$, where the detail functions of L and C are given⁸⁹ by Polley et al. Through FDTD simulation, I find that, in the case where the resonant frequency is around 0.54 THz as shown in Figs. 3-8 and 3-9 ($D_{SAR} = 10.2 \mu\text{m}$, $L_{SAR} = 40 \mu\text{m}$), enlarging (shrinking) the outer diameter D_{SAR} by $1 \mu\text{m}$ decreases (increases) the resonant frequency by about 0.02 THz. Besides, lengthening (shortening) the length of antenna L_{SAR} by $10 \mu\text{m}$ decreases (increases) the resonant frequency by about 0.01 THz. There might be a coupling between the antenna part and the solenoid (spiral-shaped) part. The existence of the solenoid part might modify the resonant frequency of the antenna part. Therefore, the antenna length is not half wavelength of the resonant frequency. How the

coupling happens and how to quantify the coupling are required to be answered in further investigation.

In this work, the SARs made of gold are fabricated on our sample surface based on Electron-Beam (EB) lithography. The strengths and the resonant frequencies of the magnetic near fields are estimated by FDTD simulation. In simulation, the refractive index of HoFeO_3 is 5.4 and the gold is regarded as a perfect metal. The sample thickness is $52 \mu\text{m}$, the optical distance of which is around half wavelength of the resonant frequency of the SAR, thus the sample itself behave as a Fabry-Pérot cavity to further increase the THz magnetic near field. By comparing with the results shown in previous studies⁹², I find that the Fabry-Pérot cavity formed by front and back sample (the orthoferrite) surfaces contributes to the Q factor of the enhancement factor, but the SAR ($D_{\text{SAR}} = 10.2 \mu\text{m}$, $L_{\text{SAR}} = 40 \mu\text{m}$) generates a relatively broadband enhancement. By simulation, the Q factor of the magnetic near field for my sample is about 9.3 and the enhancement factor is about 200 times as shown in Fig. 3-9. We find that the enhancement factor of SAR is far stronger than that of SRR.

How many Tesla the THz magnetic near fields are is also estimated by FDTD simulation. In the experiment, the single-cycle THz pulses have the peak amplitude about 0.8 MV/cm as shown in Fig. 3-10. To avoid transient overload currents destroying the resonators, a low-pass filter ($< 0.68 \text{ THz}$) is applied before the sample. The filtered THz pulse is used as the input of FDTD simulation. The calculation results of $\mathbf{B}_{\text{THz}}^{\text{NF}}(t)$ and $\mathbf{E}_{\text{THz}}^{\text{NF}}(t)$ at the center of coil

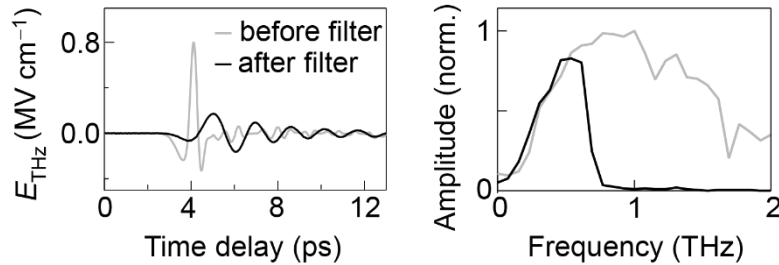


Figure 3-10. Left panel: temporal development of THz pulses Right panel: corresponding spectra. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

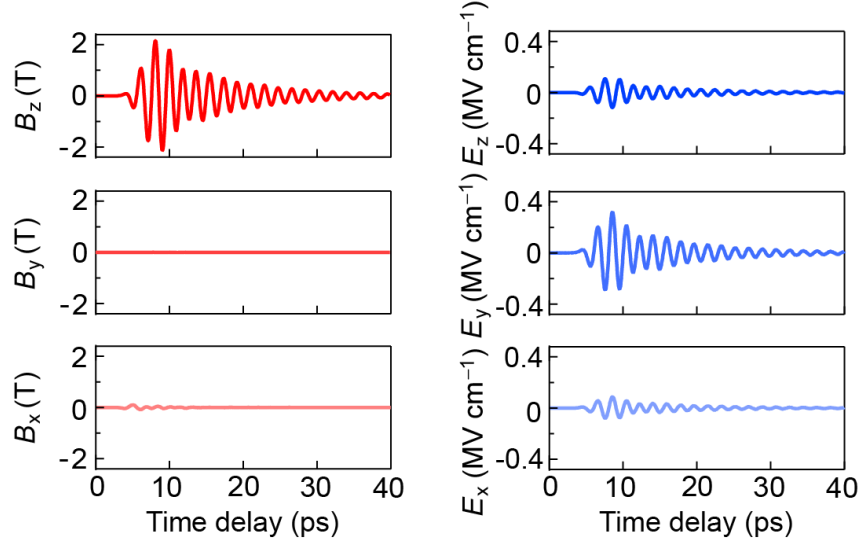


Figure 3-11. Numerical calculation results of $\mathbf{B}_{THz}^{NF}(t)$ and $\mathbf{E}_{THz}^{NF}(t)$. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

are shown in Fig. 3-11. A very strong multicycle magnetic near field along z axis with peak amplitude about 2 T is generated, while the y - and x -axes magnetic near fields are very weak and thus can be ignored. Therefore, $\mathbf{B}_{THz}^{NF}(t)$ can be regarded as $(0, 0, B_{THz}^{NF}(t))$. Besides, the electric near field is generated with the peak amplitude about less than 2 times of that of the incident THz pulse.

3.3 Detection of spin dynamics

3.3.1 Experiment setup

The experiment setup is shown in Fig. 3-12. The laser beam generated from an amplified Ti:sapphire laser (shown by a grey box) is presented by a red thick line. The beam with 99 % power is reflected by the Beam sampler for the THz generation and another beam with 1% power transmits through the Beam sampler for detection of spin dynamics.

The THz pulses are generated from the LiNbO₃ crystal using the tilted-optical-pulse-front method and are collected by a small parabolic mirror. Then,

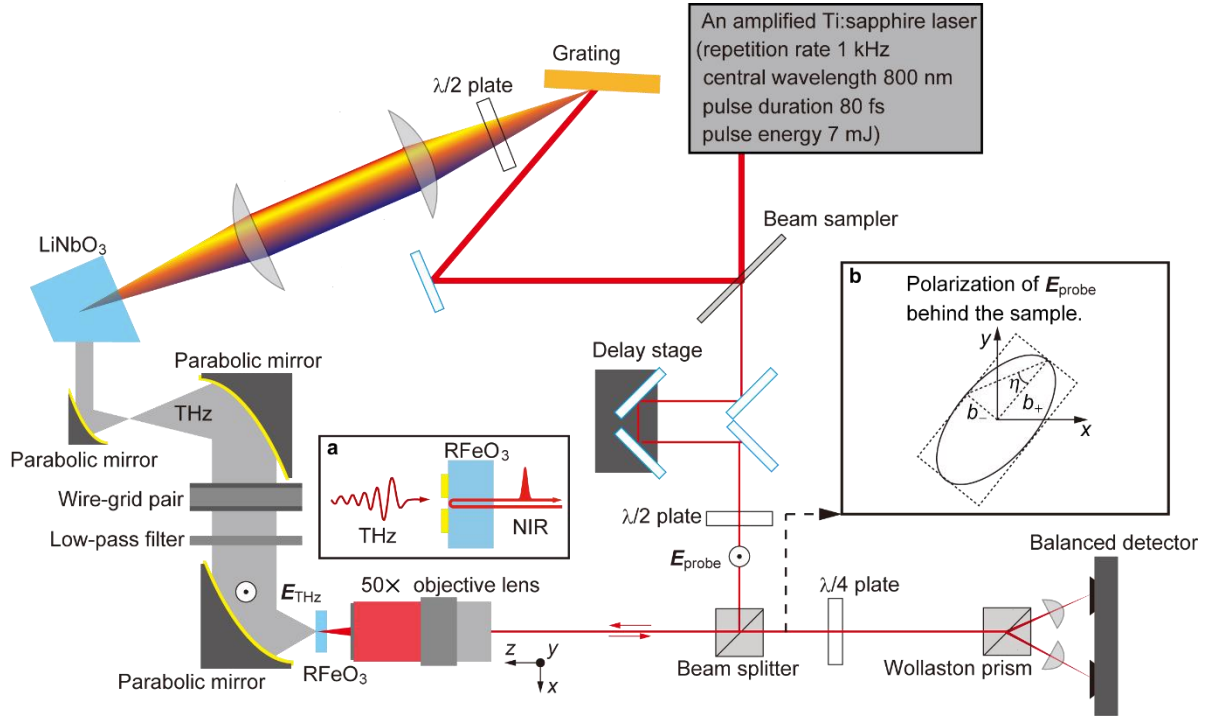


Figure 3-12. Schematic of the experiment setup. Figure reprinted with permission from the reference ⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

the beam of THz pulses is collimated and focused to the sample by two parabolic mirrors. Between the two parabolic mirrors, a wire-grid pair consisting of two wire grids is used to control the intensity of THz pulses. The wire grid is a plate wherein many thin metallic wires are aligned parallel, which allows the THz pulses with polarization perpendicular to the wires passing through the wire grid. The first wire grid is placed with wires aligned along an arbitrary direction. The second wire grid is placed with wire parallel with the paper so that the THz electric field polarized perpendicular to the paper can pass. The intensity of the THz pulses is adjusted by rotating the first wire grid.

To probe the spin dynamics at the center of the solenoid, the probe pulses were focused by an objective lens from the back surface of the sample. The spot of the probe pulse has the diameter about $1.2 \mu\text{m}$ as shown in Fig. 3-13a. The probe pulses detect a small enough area, over which the enhancement factor is almost homogeneous as shown in Fig. 3-13b. Therefore, it enables us to analyze the experimental results based on the calculation that does not consider the x - y -plane distribution of magnetic near field.

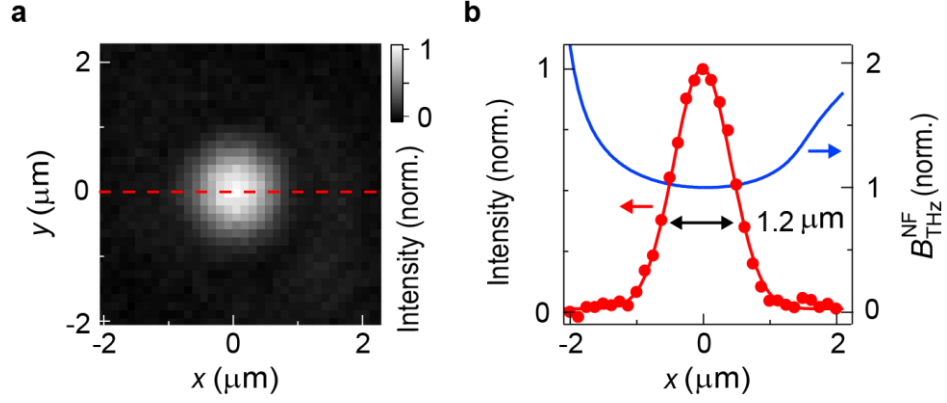


Figure 3-13. **a.** The beam spot of the probe pulse. **b.** The profile of the beam spot. The red points are the data along the red dashed line in **a**, and the red curve is a fit to a Gaussian function. The blue curve is the distribution of the magnetic near field for $y = 0$ shown in Fig. 3-9a. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

3.3.2 Detection of the ellipticity angle of probe pulses

After that the probe pulses transmit the sample and are reflected by the sample surface (Fig. 3-12a), the polarization of probe pulses becomes an ellipse with the ellipticity angle η (Fig. 3-12b). The angle between the major axis and y axis is defined by ϕ . The ellipticity angle η can be detected by the combination of a quarter wave plate, a Wollaston prism and a balanced detector. The polarization of the probe pulse before incidence is along y axis and is given by,

$$\mathbf{E}_0 = E_{\text{gate}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (3-18)$$

After leaving the sample, the ellipse polarization is given by using two rotation matrixes as well as a matrix for $-\pi/2$ phase retardance,

$$\begin{aligned}
 \mathbf{E}_1 &= E_{\text{gate}} \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -i \end{pmatrix} \begin{pmatrix} \cos(-\eta) & \sin(-\eta) \\ -\sin(-\eta) & \cos(-\eta) \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\
 &= E_{\text{gate}} \begin{pmatrix} -\cos\phi\sin\eta - i\sin\phi\cos\eta \\ \sin\phi\sin\eta - i\cos\phi\cos\eta \end{pmatrix}.
 \end{aligned} \tag{3-19}$$

A quarter wave plate is placed behind the sample and the fast axis is rotated $-\pi/4$ from y axis. The polarization of probe pulse transmitting through the wave plate is given by,

$$\begin{aligned}
 \mathbf{E}_2 &= \begin{pmatrix} \cos(-\frac{\pi}{4}) & \sin(-\frac{\pi}{4}) \\ -\sin(-\frac{\pi}{4}) & \cos(-\frac{\pi}{4}) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -i \end{pmatrix} \begin{pmatrix} \cos\frac{\pi}{4} & \sin\frac{\pi}{4} \\ -\sin\frac{\pi}{4} & \cos\frac{\pi}{4} \end{pmatrix} \mathbf{E}_1 \\
 &= \frac{E_{\text{gate}}}{2} \begin{pmatrix} -\sin(\eta + \phi) + \cos(\eta - \phi) + i(-\cos(\eta + \phi) + \sin(\eta - \phi)) \\ -\sin(\eta - \phi) - \cos(\eta + \phi) - i(\cos(\eta - \phi) + \sin(\eta + \phi)) \end{pmatrix}.
 \end{aligned} \tag{3-20}$$

The Wollaston prism is placed behind the quarter wave. The probe pulse is decomposed into the x -axis and y -axis components which are been spatially separated. Then two components are incident into the balanced detector. The ellipticity angle is given by,

$$\eta = \frac{1}{2} \arcsin \left(-\frac{I_x - I_y}{I_x + I_x} \right), \tag{3-21}$$

where I_x and I_x are the intensities of $E_{2,x}$ and $E_{2,y}$, respectively.

In the experiment, the delay stage in the beam path of the probe pulses is controlled to vary the optical distance between the probe pulses and the pump pulses, and thus the time difference between the probe pulses and the pump pulses arriving the sample can be varied. Hereafter, the time difference is

indicated by time delay t . The ellipticity angle at different time delay t is detected and indicated by $\eta(t)$. The spin dynamics which are excited by the pump pulses are probed by the changes of ellipticity angle, $\Delta\eta(t) = \eta(t) - \eta_{\text{equilibrium}}$, where $\eta(t)$ and $\eta_{\text{equilibrium}}$ are the ellipticity angles when THz pulses are applied to samples and are blocked, respectively.

Chapter 4 Second- and third-order harmonic generations of spin dynamics

In this chapter, we studied the coherent nonlinear dynamics of q-AFM mode in a HoFeO_3 crystal at room temperature. The observed time-resolved changes in the ellipticity angle clearly showed the oscillations of q-AFM mode. Under the strong excitation, the signals exhibit the frequency redshift, the second- and third-order harmonics and an asymmetric oscillation behaviour in the time domain. Not only the anharmonic potential energy of the q-AFM mode but also the magneto-optic effect related to the q-AFM mode plays an important role in these phenomena. In section 4.1, the background of the ultrafast control of q-AFM mode and the purpose of this chapter are introduced. In section 4.2, the sample fabrication and the experiment setup are introduced. The section 4.3 shows the experimental results and summarizes the three main features. The sections 4.4, 4.5 and 4.6 explain the three main features based on the motion equation of q-AFM mode and the wave equation describing the magneto-optic effect. The section 4.7 presents the numerical calculations of the two equations. The response of our sample to THz electric field is discussed in the section 4.8. Finally, we have a summary in the section 4.9.

4.1 Background

They have attempted various methods to excite the q-AFM mode with optical pulses in the range from visible to mid-infrared frequencies. The accessible methods are found to be exciting the charge-transfer transitions or exciting the circularly polarized phonon modes. The charge-transfer transitions are excited, so that the electron distribution in the cluster $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ is modified²⁴, thus leading to the ultrafast perturbation of the antiferromagnetic exchange interaction H_E and DMI H_D . The perturbation works as a transient

torque to excite the q-AFM mode. On the other hand, the circularly polarized phonon modes with lifetime < 1 ps are excited to trigger the q-AFM mode via the Barnett effect²⁵, where the circular motions of ions generate the sub-picosecond magnetic fields in the sample. The q-AFM mode is excited by the Zeeman torque of the transient magnetic fields. However, because the couplings between the spin system and the electron or phonon systems are relatively weak, it is difficult to track the nonlinear spin responses of q-AFM mode by using optical pulses.

Since the first use a decade ago, THz pulses have been considered as a more efficient means of directly exciting q-AFM mode via Zeeman torque without coupling with other degrees of freedom^{28,31,93}. One of the distinct signatures of nonlinear spin dynamics due to the anharmonic potential energy is the generation of second-harmonic (SH) or third-harmonic (TH) oscillations. However, because the maximum peak amplitude of a single-cycle THz pulse usually reaches only about 0.1 T and its spectral density at the spin resonance frequency is also limited, the harmonic spin oscillation is limited to the second order in common approaches³¹. In this study, we observed a large spin-precession amplitude of the q-AFM mode, that generates the frequency redshift and the SH and TH oscillations, in the canted antiferromagnet HoFeO₃ by using the excitation of Tesla-class THz magnetic near fields. Based on the theoretical analysis, we revealed their relations with the anharmonic potential energy of the q-AFM mode and the magneto-optic effect related to the q-AFM mode.

4.2 Sample fabrication and experimental setup

Single crystal HoFeO₃ was fabricated by Dr. Mukai of Kyoto University using the Floating zone method⁹⁴. The powder sample of HoFeO₃ is provided by Kageyama group of Kyoto University. In the Floating zone method, light from a halogen lamp is focused onto the contact point of two raw material rods (polycrystalline samples) using an elliptical mirror. The samples near the focal point are heated to their melting point. Single crystals are grown by

simultaneously moving the molten material downward. The raw material rods are placed in quartz tubes, and a constant flow of mixed air is flowed inside the tubes. To ensure uniform heating of the samples and stabilization of the molten surface, the upper and lower raw material rods are rotated in opposite directions (16 round/min), and the downward movement speed is set to 6 mm/h. The HoFeO_3 single crystal was cut perpendicular to c axis and was polished to a thickness of 52 μm . The crystallographic a , b , and c axes are parallel to the x , y and z axes, respectively. A single magnetic domain was confirmed by a two-dimensional static Kerr ellipticity measurement at zero magnetic field. At room temperature which is much higher than the SRT temperature (~ 50 K), the two magnetizations $\mathbf{m}_i$ ($i = 1, 2$) of the iron sublattices in HoFeO_3 are mainly antiferromagnetically aligned along a axis (with a slight canting angle $\beta_0 = 0.63^\circ$ due to DMI) and exhibit a spontaneous magnetization $\mathbf{M}$ along c axis.

We fabricated an array of metallic microstructures of SARs with a thickness of 200 nm on the crystal surface by an electron-beam lithographic process at Nanotechnology Hub of Kyoto University. Initially, the resist and the conductive film were sequentially spin-coated onto the sample. Subsequently, it was introduced into the electron beam chamber, where the resist underwent irradiation by a focused electron beam, scanning in the shape of SARs. The conductive film prohibited the electrons accumulating on the surface. This process rendered the irradiated portion susceptible to dissolution in the developer solution. After this, the sample was removed from the chamber and immersed in the developer, thereby revealing the resist structured in the shape

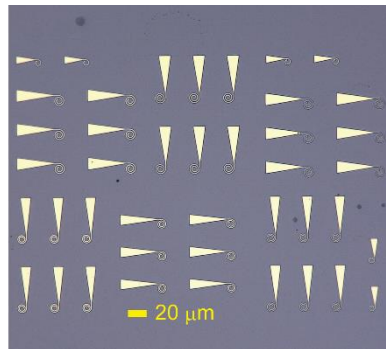


Figure 4-1. Sample photograph.

of SARs. Then, the sample was placed in an evaporator where the metallic thin films consisting of a 5-nm adhesive Cr layer and a 195-nm Au layer are deposited. Finally, the remaining resist was removed, resulting in the formation of Cr/Au in the shape of SARs on the sample. The sample photographs are shown in Fig. 4-1.

Before each experiment, we applied a bias magnetic field to the sample to saturate its magnetization along c axis. The hysteresis in the Kerr rotation plotted versus the magnetic field is shown in Fig. 4-2. The static magnetic field required to reverse the magnetization is ~ 50 mT. Regarding the experiment with the THz pulse, we need to consider that the THz magnetic field is a transient pulse with a duration on the order of picoseconds. In contrast to the result for the static magnetic field, the coherent reversal of magnetization is much more difficult in the case of such a short pulse.

In the THz region, there are two antiferromagnetic resonance modes, the so-called q-AFM mode and the q-FM mode. The magnetic near field $\mathbf{B}_{\text{THz}}^{\text{NF}}$ in our setup causes a q-AFM mode motion; as illustrated by the dashed blue curves in Fig. 4-3, the Zeeman torque exerted on the spins triggers a precession of each sublattice magnetization $\mathbf{m}_1$ and $\mathbf{m}_2$ about the equilibrium direction.

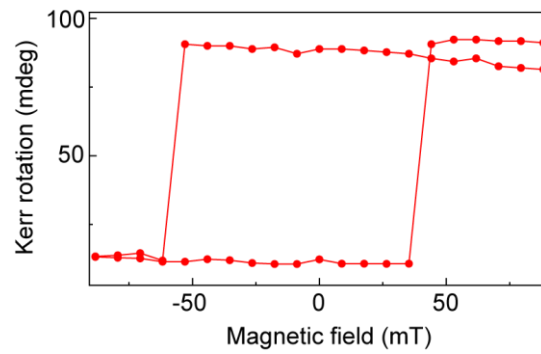


Figure 4-2. Magnetic field dependence of the Kerr rotation of HoFeO₃ at room temperature. The probe wavelength is 633 nm. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

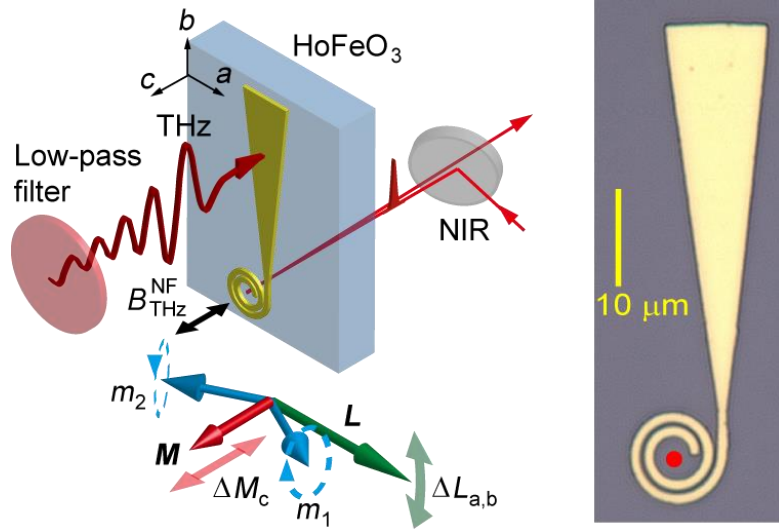


Figure 4-3. Left panel: Schematic of pump-probe measurement ($a//x$; $b//y$; $c//z$); Right panel: Photograph of a single SAR. Figure reprinted with permission from the reference ⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

This precession causes an oscillation of the ferromagnetic vector $\mathbf{M}$ in the c -axis direction and a pendulum motion of the antiferromagnetic vector $\mathbf{L}$ in a – b plane. The resultant spin dynamics are detected as the change of ellipticity angle $\Delta\eta$. We used a $50\times$ objective lens to focus linearly polarized optical probe pulses in the plane of the microstructure (spot diameter $\sim 1.2\ \mu\text{m}$), which enabled us to measure local changes in the ellipticity angle change $\Delta\eta$. Note that the HoFeO_3 crystal was sufficiently transparent for the used NIR probe pulses (800 nm). The polarization directions of the THz light and the probe light were parallel and almost along b axis. A balanced detector combined with a quarter-wave plate and a Wollaston prism was used to measure the ellipticity angle of the reflected probe pulse.

4.3 Experimental result

The three temporal profiles of the changes in the ellipticity angle ($\Delta\eta$) are shown in in Fig. 4-4 for THz electric-field amplitudes equal to $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$, 0.55 MV cm^{-1} and 0.2 MV cm^{-1} (E_{THz} is measured without filter). The corresponding amplitudes of THz magnetic near fields at the sample

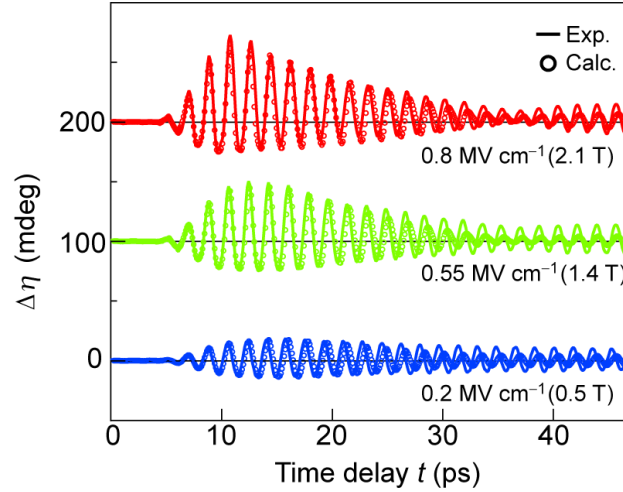


Figure 4-4. THz-pump-induced ellipticity-angle change $\Delta\eta$. The red, green, and blue curves show the observed time-domain signals $\Delta\eta$ for THz pulses with $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$, 0.55 MV cm^{-1} and 0.2 MV cm^{-1} , respectively. The red and green curves are offset for clarity. The open circles are the corresponding results calculated by using the motion equation of q-AFM mode and considering the magneto-optic effect. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

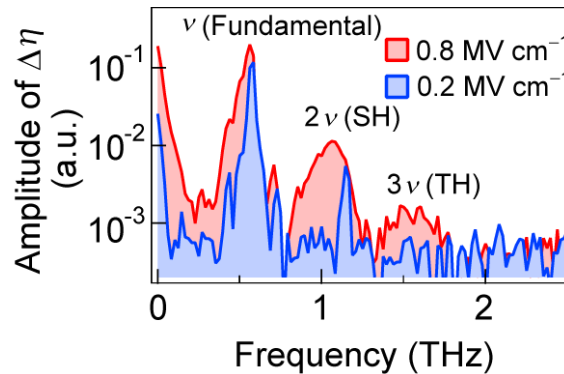


Figure 4-5. The red and blue spectra are the Fourier spectra of the experimental data obtained using $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$ and 0.2 MV cm^{-1} , respectively. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

surface are $B_{\text{amp}}^{\text{NF}} = 2.1 \text{ T}$, 1.4 T and 0.5 T ($B_{\text{amp}}^{\text{NF}}$ is calculated by FDTD simulation with filter). The time moment of THz pulse arriving sample can be determined based on THz Kerr effect introduced in section 4.8. This time moment is set at 5.1 ps by hand in this chapter 4.

The curve for $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$ exhibits a distorted sinusoidal oscillation with an asymmetric envelope, i.e., the amplitudes of the signals with $\Delta\eta > 0$ are larger than those of the signals with $\Delta\eta < 0$. The spectra are obtained by Fourier transformation and are shown in Fig. 4-5. For weak excitation with $E_{\text{THz}} = 0.2 \text{ MV cm}^{-1}$, the fundamental peak is at $\nu = \nu_{\text{AFM}} \approx 0.58 \text{ THz}$ and is consistent with the previous report, which indicates that the

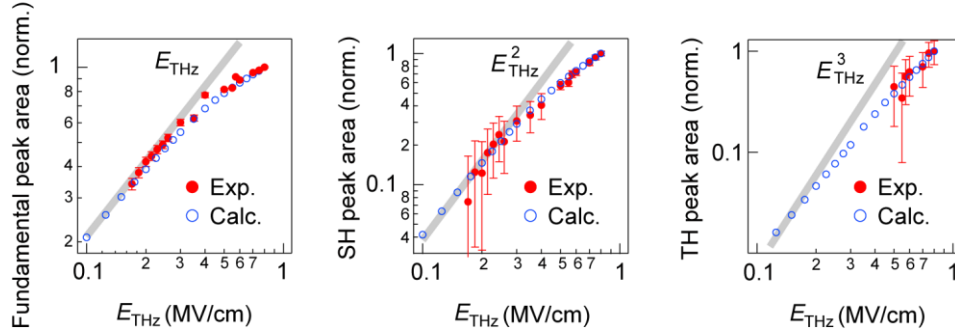


Figure 4-6. Field-strength dependence for the fundamental, SH and TH peak areas. The open circles are the corresponding results calculated by using the motion equation of the q-AFM mode and considering the magneto-optic effect. The error bars represent the noise floor in the spectra, which is obtained by integrating the spectral amplitudes of the case for $E_{\text{THz}} = 0.2 \text{ MV cm}^{-1}$ over the range from 1.25 THz to 1.71 THz . Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

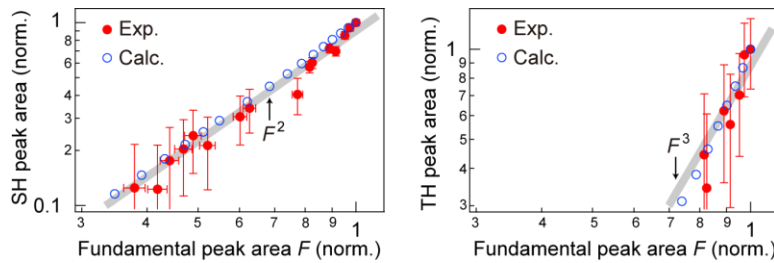


Figure 4-7. Field-strength dependence for the SH and TH peak areas. Data are same as these in Fig. 4-6. The horizontal axis is the fundamental peak area F . Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

oscillation in Fig. 4-4 is attributed to the q-AFM mode. Apart from the fundamental peak at ν_{AFM} , the peaks at precise $2\nu_{\text{AFM}}$ can be found which is attributed to the second-order harmonic of q-AFM mode. For the strong excitation with $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$, the spectrum exhibits the second-order-harmonic (SH) and the third-order-harmonic (TH) peaks. Interestingly, the fundamental peak shows a remarkable broadening towards low-frequency side. Meanwhile, the center frequencies of the SH and TH peaks (1.06 THz and 1.58 THz) are lower than $2\nu_{\text{AFM}}$ (1.16 THz) and $3\nu_{\text{AFM}}$ (1.74 THz).

The dependences on the field strength of the three peaks are shown in Fig. 4-6. The data points are the peak areas obtained by integrating the corresponding peaks in the spectra. The grey lines are proportional to the first, second, and third power of E_{THz} . The error bars represent the noise floor in each spectrum. We found that the field-strength dependences of these peaks deviate from the power law of the electric (magnetic) field. It is attributed to the nonlinear damping of spin dynamics where the damping becomes stronger as the oscillation amplitude becomes stronger. However, when the SH and TH amplitudes are plot as the functions with respect to the amplitude of the fundamental peak, as shown in Fig. 4-7, the power law scaling can be confirmed, which is same as the high-order harmonic generation in the electron system. Be superior to regarding harmonic peaks as the function of the pump field, the amplitude of fundamental peak directly reflects the strength of the spin precession. The power law scaling confirms that the SH and TH peaks originate from the nonlinearities of the spin precession.

Here we summarize three main features exhibited by the experimental results: (i) the asymmetric amplitude of oscillation observed in the time domain (Fig. 4-4), which is called DC component, (ii) the SH and TH generations in the frequency region (Fig. 4-5), (iii) the broadening of spectral peaks towards low-frequency side (Fig. 4-5), which is called redshift. These features will be explained in the following combined with the theoretical calculation.

4.4 Origin of redshift

4.4.1 Quantitative evaluation of redshift

To quantitatively evaluate the redshift, we performed the time-resolved Fourier transformation to $\Delta\eta(t)$ where $\Delta\eta(t)$ multiplied by a time window (a Gaussian function centered at t' with a width of 5 ps) is Fourier transformed. The spectra with different t' are shown in Fig. 4-8a. The peak frequency of the fundamental peak at different t' is read from the colormap and is plot in Fig. 4-8b. We find that the peak frequency exhibits a remarkable red shift at about 10 ps and the minimum value is indicated by $\nu_{\text{redmax}} = 0.53$ THz, where ν_{redmax} is called the redshift frequency. For excitation with $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$, the signals of the SH and TH peaks only appear around 10 ps which rise and decay with a very fast speed. Therefore, SH and TH should have the central frequencies at $2\nu_{\text{redmax}} = 1.06$ THz and $3\nu_{\text{redmax}} = 1.59$ THz, respectively, which is consistent with the observation in Fig. 4-5. As the oscillation amplitude of $\Delta\eta(t)$ decreases after 30 ps, the oscillation frequency returns to the intrinsic frequency of the q-AFM mode.

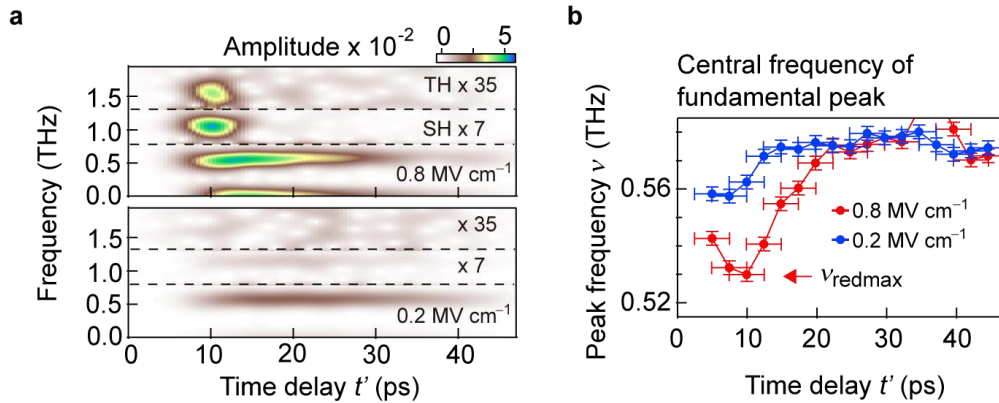


Figure 4-8. **a**, Color maps of the time-resolved Fourier-transform spectra of $\Delta\eta(t)$ for $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$ (upper panel) and 0.2 MV cm^{-1} (lower panel). The time window used for this calculation is a Gaussian function centered at t' with a width of 5 ps and all color maps use the same color scale. **b**, Temporal variation of the oscillation frequency obtained from the spectral position of the fundamental peak in each time slice for the data (red: 0.8 MV cm^{-1} , blue: 0.2 MV cm^{-1}) in **a**. Figure reprinted with permission from the reference ⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

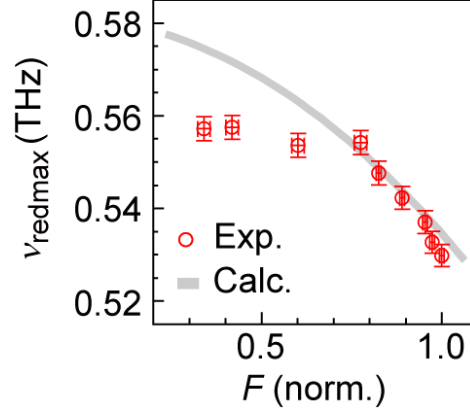


Figure 4-9 Field-strength dependence of ν_{redmax} . The red circles are the experimentally obtained value. The grey curve is the calculation result of Eq. (4-8) as the function of $k\varphi_{\text{max}}$, where k is set to 1.8 rad^{-1} .

We plot the redshift frequency ν_{redmax} as a function of the fundamental peak area F under different field strengths in Fig. 4-9. We find that the result exhibits two stages. Firstly, when the excitation is relatively weak (F is smaller than 0.8), ν_{redmax} almost does not change. This is attributed to the forced oscillation driven by the THz magnetic near field where the frequency of the THz magnetic near field is a bit lower than the intrinsic frequency of q-AFM mode. From the experimentally obtained ν_{redmax} , we can estimate the frequency of the THz magnetic near field is about 0.56 THz. Secondly, when the excitation becomes strong (F is larger than 0.8), ν_{redmax} starts to decrease, which cannot be explained by the forced oscillation. In the following, we will discuss why the decrease happens.

4.4.2 Explanation of redshift based on LLG equations

The lower redshift frequency under stronger excitation is attributed to the anharmonic potential energy of the q-AFM mode. The analysis is presented in the following. The result of LLG equations, Eq. (2-20), is used here,

$$\dot{\mathbf{L}} \times \mathbf{H}_D + \dot{\mathbf{B}} - \dot{\mathbf{L}}(\mathbf{B} \cdot \mathbf{L}) - \mathbf{L}(\dot{\mathbf{B}} \cdot \mathbf{L} + \mathbf{B} \cdot \dot{\mathbf{L}}) + \frac{\dot{\mathbf{L}} \times \mathbf{L}}{\gamma} = \quad (4-1)$$

$$-\gamma(\mathbf{L} \times \mathbf{H}_D) \times \mathbf{B} + \gamma(\mathbf{B} \cdot \mathbf{L})\mathbf{L} \times \mathbf{B} - (\dot{\mathbf{L}} \times \mathbf{L}) \times \mathbf{B} + 2H_E\gamma\mathbf{L} \times \frac{\partial V}{\partial \mathbf{L}}.$$

$$V = H_E \mathbf{M}^2 - \mathbf{M} \cdot (\mathbf{L} \times \mathbf{H}_D + \mathbf{B})$$

$$-A_{aa}L_a^2 - A_{cc}L_c^2 + A_4(L_a^4 + L_b^4 + L_c^4). \quad (4-2)$$

We can ignore the term of A_4 here because the value is far smaller than A_{aa} . In our experiment, magnetic field $\mathbf{B}$ ($= \mathbf{B}_{\text{THz}}^{\text{NF}}$) and magnetization $\mathbf{M}$ are both oriented along $c(z)$ axis, and thus only q-AFM mode can be excited. It is confirmed in Fig. 4-5 where the q-FM mode (at 0.37 THz) is absent. As introduced in section 2.3 that the q-AFM mode corresponds to the swing motion of vector $\mathbf{L}$ perpendicular to a - $c(x$ - $z)$ plane, $\mathbf{L}$ can be defined by (Fig. 4-10),

$$\mathbf{L} = (L_0 \cos \varphi, L_0 \sin \varphi, 0), \quad (4-3)$$

where the length L_0 is regarded as a constant ($L_0 = 1$). Because of the vanishing c -axis component of $\mathbf{L}$, the LLG equations becomes,

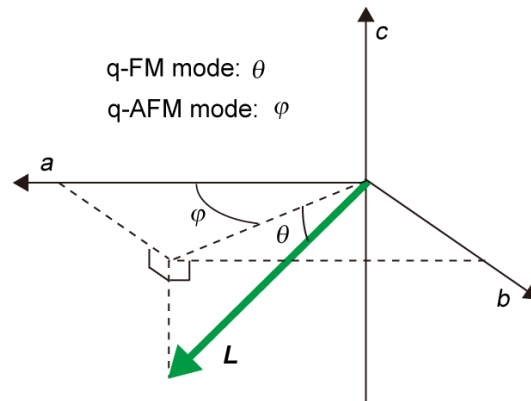


Figure 4-10. The definition of the sphere coordinates of $\mathbf{L}$. At equilibrium state, φ is equal to zero, and θ is determined by the anisotropy interactions. In this experiment, θ remains at 0.

$$\frac{\dot{\mathbf{L}} \times \mathbf{L}}{\gamma} = -\dot{\mathbf{L}} \times \mathbf{H}_D - \dot{\mathbf{B}}_{\text{THz}}^{\text{NF}} + 2H_E \gamma \mathbf{L} \times \frac{\partial V}{\partial \mathbf{L}}, \quad (4-4)$$

By inserting Eq. (4-3) into Eq. (4-4) and using Eq. (2-19), we obtain the motion equation of φ ,

$$\ddot{\varphi} = \gamma \dot{B}_{\text{THz}}^{\text{NF}} - \gamma^2 H_D^2 \sin \varphi \cos \varphi - 4H_E \gamma^2 A_{aa} \cos \varphi \sin \varphi, \quad (4-5)$$

When we adopt the linear approximation, φ behaves as a harmonic oscillator,

$$\ddot{\varphi} = \gamma \dot{B}_{\text{THz}}^{\text{NF}} - \gamma^2 (H_D^2 + 4H_E A_{aa}) \varphi, \quad (4-6)$$

and the intrinsic frequency is given by, $\omega_{\text{AFM}}^2 = \gamma^2 (H_D^2 + 4H_E A_{aa})$, where $\omega_{\text{AFM}} = 2\pi\nu_{\text{AFM}}$. The frequency can also be obtained by simplifying Eq. (2-12). When the q-AFM mode was excited with a large amplitude, the linear approximation would fail. The potential energy is given in an anharmonic form,

$$W_{\text{AFM}} = \frac{\omega_{\text{AFM}}^2}{2} \sin^2 \varphi. \quad (4-7)$$

The restoring forces $|-dW_{\text{AFM}}/d\varphi|$ in the anharmonic and harmonic potential energies are $|\omega_{\text{AFM}}^2 \sin \varphi \cos \varphi|$ and $|\omega_{\text{AFM}}^2 \varphi|$, respectively. Obviously, for nonzero φ , the restoring force in the anharmonic potential energy is weaker. Therefore, the period of motion in the anharmonic potential energy (under strong excitation) is longer than that in the harmonic potential energy (under weak excitation), which leads to the frequency redshift.

Under the intense excitation, the frequency of the motion equation is solved, by using energy conservation law, as the function with respect to the oscillation amplitude φ_{max} of q-AFM mode,

$$\nu_{\text{redmax}} = \left[\int_0^{\varphi_{\text{max}}} \frac{4}{\sqrt{\omega_{\text{AFM}}^2 \sin^2 \varphi_{\text{max}} - \omega_{\text{AFM}}^2 \sin^2 \varphi}} d\varphi \right]^{-1}. \quad (4-8)$$

Because the oscillation amplitude of q-AFM mode obtained by experiment can be evaluated by the peak area F , we assume F is equal to $k\varphi_{\text{max}}$, where k is a constant. ν_{redmax} is plotted as the function of $k\varphi_{\text{max}}$ in Fig. 4-9. It can well reproduce the decrease of ν_{redmax} obtained by experiment. Therefore, we can conclude the anharmonicity contributes to the decrease of the redshift frequency.

By inserting the experimentally obtained redshift frequency $\nu_{\text{redmax}} = 0.53$ THz into Eq. (4-8), we can estimate the deflection angle of vector $\mathbf{L}$, φ_{max} ,

$$\varphi_{\text{max}} \approx 34^\circ. \quad (4-9)$$

The redshift can also be understood using quantum mechanics as shown in Fig. 4-11. The quantization of the oscillation of magnetic order is called

Energy level of the magnon system:

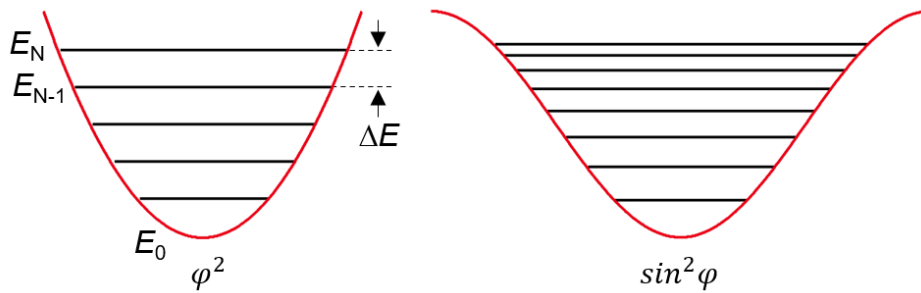


Figure 4-11. The energy level of the magnon system with a harmonic (left) and anharmonic (right) potential energy. The number of magnons at the excited state is defined by N . The black line indicates the total energy of magnons which also refers to the energy level E_N of the magnon system. The energy gap between adjacent levels is defined by ΔE .

magnon. If the oscillation is dominated by a harmonic potential energy $\omega_{\text{AFM}}^2 \varphi^2 / 2$, the energy level of the magnon system is given by $E_N = (1/2 + N)\hbar\omega_{\text{AFM}}$, where $N = 0, 1, 2, \dots$ refers to the number of magnons. The energy of one magnon is a constant $\hbar\omega_{\text{AFM}}$ and does not vary with the magnon number. However, if the oscillation is dominated by $\omega_{\text{AFM}}^2 \sin^2 \varphi / 2$, the energy level of the magnon system is smaller than $(1/2 + N)\hbar\omega_{\text{AFM}}$. Meanwhile, the energy gap ΔE between adjacent levels decreases with the increase of N . Therefore, the energy of one magnon is smaller than $\hbar\omega_{\text{AFM}}$ and decreases with the increase of N . The similar phenomena were also observed in the lattice system where the frequency shifts of phonon modes are induced by the strong excitation of lattice vibration^{95,96}.

4.5 Origin of the third-order harmonic

The anharmonic potential energy, $W_{\text{AFM}} = (1/2)\omega_{\text{AFM}}^2 \sin^2 \varphi$, is also the reason of the generation of the odd-order harmonics. The phenomenon can be explained by an analysis shown in the following, which is similar with the Rayleigh-Schrödinger perturbation theory in quantum mechanics⁶⁵. We consider the motion equation of q-AFM mode perturbed by a force as the δ function,

$$\ddot{\varphi} = -\omega_{\text{AFM}}^2 \cos \varphi \sin \varphi + \lambda \delta(t), \quad (4-10)$$

where λ is the perturbation strength. The solution of Eq. (4-10) for $t > 0$ is assumed to have the form of a power-series expansion with respect to λ ,

$$\varphi = \lambda \varphi^{(1)} + \lambda^2 \varphi^{(2)} + \lambda^3 \varphi^{(3)} + \dots \quad (4-11)$$

Therefore, the terms in Eq. (4-11) proportional to λ , λ^2 and λ^3 satisfy the following equations separately,

$$\ddot{\varphi}^{(1)} = -\omega_{\text{AFM}}^2 \varphi^{(1)}, \quad (4-12a)$$

$$\ddot{\varphi}^{(2)} = -\omega_{\text{AFM}}^2 \varphi^{(2)}, \quad (4-12b)$$

$$\ddot{\varphi}^{(3)} = -\omega_{\text{AFM}}^2 \left(\varphi^{(3)} - \frac{2}{3} \varphi^{(1)3} \right), \text{ etc.} \quad (4-12c)$$

We find that $\varphi^{(1)}$ and $\varphi^{(2)}$ has an intrinsic angular frequency at ω_{AFM} , and the frequency of $\varphi^{(3)}$ is three times of ω_{AFM} . If the equations are expanded to higher orders, the terms oscillating at odd-order multiples of the intrinsic frequency can be obtained. Therefore, we conclude that the anharmonic potential energy leads to the odd-order harmonic generation. Further, it is obvious that the analysis here based on the perturbative approximation (Eq. (4-11)) does not explain the redshift of the q-AFM mode, thus indicating the redshift is a non-perturbative phenomenon.

In addition, W_{AFM} has the inversion symmetry with respect to φ , and thus is not responsible for the DC component and the even-order harmonics.

4.6 Origin of the DC component and second-order harmonic

The DC component and the even-order harmonics shown by $\Delta\eta(t)$ are attributed to the magneto-optic effect. In our experiment, due to the magneto-optic effect, the polarization states of probe pulses leaving the sample are changed by the spin dynamics. The change in ellipticity angle $\Delta\eta(t) = \eta(t) - \eta_{\text{equilibrium}}$ is detected, where η and $\eta_{\text{equilibrium}}$ are the ellipticity angles when spin dynamics are excited and not excited, respectively. To describe the magneto-optic effect, we consider the propagation of the electric field of the probe light in HoFeO₃. The plane-wave equation along $c(z)$ axis in the sample⁵⁹ is given by,

$$\mu \begin{pmatrix} \varepsilon + \sigma & i\kappa \\ -i\kappa & \varepsilon - \sigma \end{pmatrix} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{\partial^2 \mathbf{E}}{\partial z^2}, \quad (4-13)$$

$$\kappa = f \cdot \frac{M_0 + \Delta M_c}{M_0} + g \cdot \frac{L_0 + \Delta L_a}{L_0}, \quad (4-14)$$

where μ , ε and σ are constants independent of the magnetization. ΔM_c is the temporal variation of the c -axis component of the ferromagnetic vector $\mathbf{M}$, and ΔL_a is the temporal variation of the a -axis component of the antiferromagnetic vector $\mathbf{L}$. M_0 and L_0 are the amplitudes of $\mathbf{M}$ and $\mathbf{L}$ at equilibrium ($L_0 = 1$). The phenomenological parameters f and g represent the contributions of ferromagnetic and anti-ferromagnetic vectors to the off-diagonal elements, respectively. Here, we ignored the symmetric terms in the off-diagonal elements which is the origin of the Cotton-Mouton effect, because this effect is negligible for the probe wavelength of 800 nm in the rare-earth orthoferrites⁵⁶.

The variables ΔL_a and ΔM_c can be written as the functions with respect to φ . The function of ΔL_a is given by,

$$\Delta L_a = 1 - \cos\varphi. \quad (4-15)$$

The vector $\mathbf{M}$ is a slave variable determined by the vector $\mathbf{L}$. According to Eq. (2-19), we obtain,

$$\Delta M_c = \frac{1}{2H_E} \left[-\frac{\dot{\varphi}}{\gamma} + H_D(\cos\varphi - 1) \right]. \quad (4-16)$$

The THz magnetic near field is ignored, because it is much smaller than H_D . We found both ΔL_a and ΔM_c have the term of $\cos\varphi$, where $\cos\varphi$ can be expanded to the even-order terms of φ , $\cos\varphi = 1 - \varphi^2/2 \dots$. Because φ is verified oscillating at the odd-order multiples of the intrinsic frequency, $\cos\varphi$ must oscillate at the even-order multiples of the intrinsic frequency and have a

DC component. Therefore, we conclude that the DC component and the even-order harmonics shown by $\Delta\eta(t)$ are attributed to the magneto-optic effect.

4.7 Numerical calculations

In the following, we will use numerical calculations to verify the contribution of the magneto-optic effect to the DC component and the second-order harmonic. We numerically solved Eq. (4-5) to obtain the dynamics of φ and then inserted the solutions to Eqs. (4-15) and (4-16) to obtain the dynamics of ΔL_a and ΔM_c . Finally, the propagation equation of the probe pulse is solved to calculate the magneto-optic effect of probe pulse occurring in the sample.

4.7.1 Calculation procedure

In this calculation, the 52- μm -thick crystal is divided into 260 cells along $c(z)$ axis, and the variation of polarization of probe pulse in each cell is calculated. In each cell, the temporal evolution of magnetic field has been prepared by the FDTD simulation. The z dependence of the peak amplitude of the magnetic near field, $B_{\text{amp}}^{\text{NF}}(z)$, is shown in Fig. 4-12. The spin dynamics have been calculated by Eqs. (4-5), (4-15) and (4-16). Here, a nonlinear damping factor c is introduced to the Eq. (4-5), and thus we obtain,

$$\ddot{\varphi} + c\dot{\varphi} = \gamma\dot{B}_{\text{THz}}^{\text{NF}} - \gamma^2 H_{\text{D}}^2 \sin\varphi \cos\varphi - 4H_{\text{E}}\gamma^2 A_{aa} \cos\varphi \sin\varphi, \quad (4-17)$$

where $c = 2\gamma H_{\text{E}}\alpha_{\text{LLG}}$ and $\alpha_{\text{LLG}} = \alpha_0 + \alpha_1|\dot{\varphi}/\gamma H_{\text{D}}|$. The nonlinear term $\alpha_1|\dot{\varphi}/\gamma H_{\text{D}}|$ can be attributed to the four-magnon scattering process, which is thought to be the dominant microscopic spin scattering mechanism in a rare-earth ferrite⁹⁷. This term is considered to be the reason for the saturation of the fundamental, SH and TH peak areas at stronger fields as shown in Fig. 4-6.

The spin dynamics contribute to the permittivity tensor in each cell, and by using Eq. (4-13) we calculate the propagation of the electric field of the probe light in HoFeO₃. We consider that the electric field $\mathbf{E}$ of the probe pulse has the following form of a plane wave:

$$\mathbf{E} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} e^{i(\omega t - kz)}. \quad (4-18)$$

The normal modes of Eq. (4-13) are

$$\mathbf{n}_+ = \begin{pmatrix} 1 \\ i(\Gamma - \sqrt{1 + \Gamma^2}) \end{pmatrix} e^{i(\omega t - k_+ z)}, \quad (4-19a)$$

$$\mathbf{n}_- = \begin{pmatrix} 1 \\ i(\Gamma + \sqrt{1 + \Gamma^2}) \end{pmatrix} e^{i(\omega t - k_- z)}, \quad (4-19b)$$

where k_+ and k_- are defined as

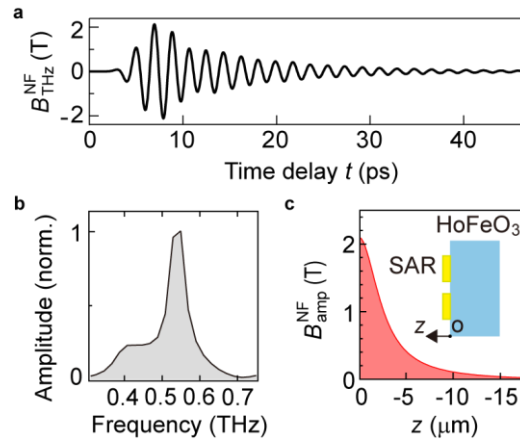


Figure 4-12. **a**, the temporal development of THz magnetic near field at the surface of the sample and at the center of the coil part of a resonator. **b**, the spectrum of the curve in **a**. **c**, Depth dependence of the maximum peak amplitude of the curve in **a**. The HoFeO₃ surface including the microstructures is located at $z = 0$. Figure reprinted with permission from the reference ⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

$$k_{\pm} = \sqrt{\omega^2 \mu (\varepsilon \pm \sqrt{\sigma^2 + \kappa^2})}, \quad (4-20)$$

and $\Gamma = \sigma/\kappa$ indicates the relative strength of the birefringence with respect to the magneto-optic effect. Any electric field in the material can be expressed by a combination of the two normal modes, that is,

$$\mathbf{E}(z_0, t_0) = \alpha_+(z_0, t_0) \mathbf{n}_+ + \alpha_-(z_0, t_0) \mathbf{n}_-. \quad (4-21)$$

After the propagation over a distance d , which is the length of one cell, the electric field becomes,

$$\begin{aligned} \mathbf{E}(z_0 + d, t_0 + \tau) &= e^{i(\omega\tau - k_+d)} \alpha_+(z_0, t_0) \mathbf{n}_+ + e^{i(\omega\tau - k_-d)} \alpha_-(z_0, t_0) \mathbf{n}_- \\ &\propto \alpha_+(z_0, t_0) \mathbf{n}_+ + e^{2i\delta d} \alpha_-(z_0, t_0) \mathbf{n}_-, \end{aligned} \quad (4-22)$$

where $\delta = (k_+ - k_-)/2$ represents the wave-vector mismatch between the two normal modes. When the probe pulse reaches the HoFeO₃ surface with the microstructures, it is reflected by the air/HoFeO₃ interface and then passes through the sample again. The reflection of the electric field at the surface is described by,

$$\begin{aligned} \mathbf{E}_r &= r_+ \alpha_+ \mathbf{n}_+ + r_- \alpha_- \mathbf{n}_- = \frac{1 - N_+}{1 + N_+} \alpha_+ \mathbf{n}_+ - \frac{1 - N_-}{1 + N_-} \alpha_- \mathbf{n}_- \\ &\propto \alpha_+ \mathbf{n}_+ + \frac{1 + N_+ - N_- - N_+ N_-}{1 - N_+ + N_- - N_+ N_-} \alpha_- \mathbf{n}_-, \end{aligned} \quad (4-23)$$

where $N_{\pm} = ck_{\pm}/\omega$.

The values of the parameters used in our solution of motion equation and calculation of magneto-optic effect are those reported in the literature^{45,58,98}, and are summarized in the following Table 4-1. We used the values⁵⁸ of YFeO₃ as f and g , because the magneto-optic effect in rare-earth orthoferrites is determined by electron transitions in Fe–O clusters and is influenced only slightly by the type of the rare-earth ion. We used the value Γ of 26 to obtain oscillation amplitudes in agreement with the experimental results, which is similar to the value of 32 in the literature⁹⁸. Here, finally, the obtained electric field $\mathbf{E}$ of the probe light is used to derive the major axis b_+ and minor axis b_- according to the following equation:

$$b_{\pm} = \sqrt{|E|^2 + 2\text{Im}(E_x^* E_y)} \pm \sqrt{|E|^2 - 2\text{Im}(E_x^* E_y)}. \quad (4-24)$$

The ellipticity angle η is calculated by $\eta = \arctan(b_-/b_+)$.

Table 4-1 The parameters used in our calculation.

Parameter	Value ^{45,58,98}
H_E	640 T
H_D	14 T
A_{aa}	8.8×10^{-2} T
A_{cc}	1.9×10^{-2} T
α_0	2.27×10^{-4}
α_1	1×10^{-3}
Γ	26
δ	2.7×10^5 rad/m
f	1×10^{-3}
g	$3 \times 10^{-3} \times e^{-i\frac{\pi}{4}}$

4.7.2 Calculation results

We show the results of numerical calculation for different field strengths in Fig. 4-4, and find that our model reproduces the asymmetric behavior well. The dependences on the pump amplitude of the three peaks are shown in Fig. 4-6, and reproduce the saturation behavior well, which indicates that the nonlinear damping term in Eq. (4-17) is important to the occurrence of the saturation behavior. The good agreement between the experiment and the calculation allows us to understand the influence of the magneto-optic effect.

To confirm the origins of DC component, and second-order harmonics, we fixed $\cos\varphi = 1$ and performed the whole calculation again. We compare the results based on the conditions ($\cos\varphi$ fixed and not fixed) in Fig. 4-13. It is obvious when $\cos\varphi$ is fixed to 1, the oscillation waveform is symmetric, and only the fundamental peak and the third-order harmonic peak can be observed. When $\cos\varphi$ is not fixed, the oscillation waveform is asymmetric (DC component exists) and the second-order harmonic peak can be confirmed. The comparison verifies that the magneto-optic effect ($\cos\varphi$ in ΔM_c and ΔL_a) is the origin of the DC component and the second-order harmonic.

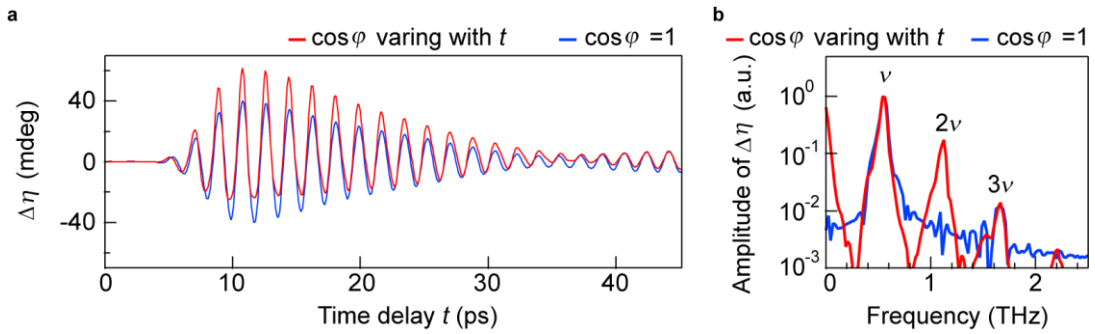


Figure 4-13. Calculation results with $\cos\varphi$ fixed and not fixed. **a**, The red and blue curves are the temporal developments of $\Delta\eta$ with $\cos\varphi$ not fixed and fixed, respectively. **b**, The corresponding spectra of the curves in **a**.

4.7.3 Estimation of the magnetization change

The calculated dynamics of $\Delta M_c/M_0$ and $\Delta L_a/L_0$ are presented in Fig. 4-14. As predicted by $\Delta M_c/M_0 = \cos\varphi - 1 - \dot{\varphi}/(\gamma H_D)$, $\Delta M_c/M_0$ exhibits an asymmetric shape of oscillation but a symmetric amplitude: the ring of oscillation for $\Delta M_c/M_0 > 0$ is sharper than $\Delta M_c/M_0 < 0$. But, $\Delta L_a/L_0$ shows a vertically asymmetrical behaviour, which is predicted by the function of $1 - \cos\varphi$. The field-strength dependences of their maximum values ($\Delta M_c^{\max}/M_0$, $\Delta L_a^{\max}/L_0$, and φ) are presented in Fig. 4-15. $\varphi_{\max}$ and $\Delta M_c^{\max}/M_0$ depend on the field amplitude almost linearly, while $\Delta L_a^{\max}/L_0$ is a cosine function of the field strength. The data points indicated by the black arrows in Fig. 4-15 represent the values calculated with the electric fields used in the experiment. From the results, we determine $\varphi_{\max} \approx 40^\circ$, $\Delta M_c^{\max}/M_0 \approx 0.9$, and $\Delta L_a^{\max}/L_0 \approx 0.2$ at the surface of HoFeO₃ for $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$. The value $\varphi_{\max} \approx 40^\circ$ is similar as the estimation using Eq. (4-8) and the experimentally

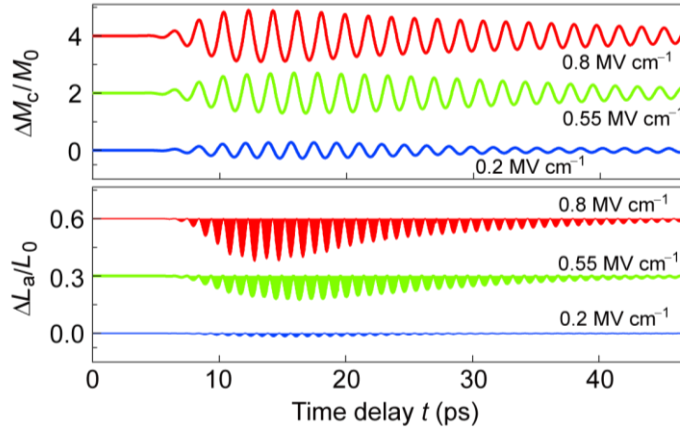


Figure 4-14. Calculated dynamics of $\Delta M_c/M_0$ (upper panel) and $\Delta L_a/L_0$ (lower panel) based on Eqs. (4-5), (4-15) and (4-16). The red and green curves are offset for clarity. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

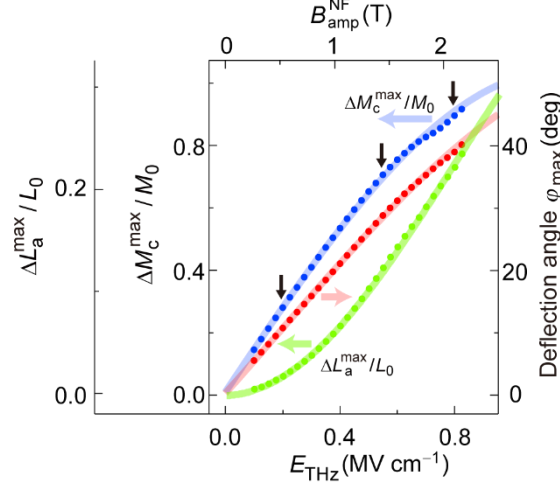


Figure 4-15. Calculated E_{THz} dependence of φ_{max} (red points), $\Delta M_c^{\text{max}}/M_0$ (blue points) and $\Delta L_a^{\text{max}}/L_0$ (green points). The black arrows indicate the results for $E_{\text{THz}} = 0.8 \text{ MV cm}^{-1}$, 0.55 MV cm^{-1} and 0.2 MV cm^{-1} , respectively. The solid curves are guides to the eye. The results are the numerical calculations of Eqs. (4-5), (4-15) and (4-16) at the HoFeO_3 surface including the microstructure. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

obtained redshift frequency ν_{redmax} , indicating the numerical calculation is rational. The overestimation of φ_{max} here based on numerical calculation is possibly due to the overestimation of the amplitude of the magnetic near field using FDTD simulation.

4.8 Effect of THz electric field

In the following, we exclude the possibility that the asymmetric waveform is a result of the THz Kerr effect. The THz Kerr effect is attributed to the third-order nonlinear susceptibility modified by THz electric field and is magnetism independent. The signal due to THz Kerr effect should not depend on the sign of the magnetization, but our measured $\Delta\eta$ induced by THz magnetic near field depends on the sign as shown in Fig. 4-16a. Here we reverse the magnetization $\mathbf{M}$ along c axis by reversing the bias magnetic field.

To confirm the Kerr effect induced by THz electric field does not depend on

the sign of the magnetization, we performed another experiment. As shown in Fig. 3-11 in the section 3.2.4, the electric field in the center of the microstructure is $\sim 0.3 \text{ MV cm}^{-1}$ along b axis. In the additional experiment, a THz electric pulse polarized along b axis with a peak amplitude of about 1 MV cm^{-1} was directly incident on a sample without microstructures. Considering the reflection loss, the electric field of this propagating THz pulse (not near field) in HoFeO_3 is 0.31 MV cm^{-1} . The result of the experiment is shown in Fig. 4-16b: no oscillating signal is observed other than a very small double peaks at about 5 ps (the moment where THz pulses arrive at the sample). The small peaks are due to the THz Kerr effect which tracks the square of the THz pulse^{30,99}. It is observed that the sign of THz Kerr signal does not depend on the direction of $\mathbf{M}$. Therefore, we can confirm that the asymmetric waveform in Fig. 4-16a is not a result of the THz Kerr effect. The mechanism enables us to determine the time moment when THz pulse arrives the sample.

We can also exclude thermally induced changes in the spin structure. The

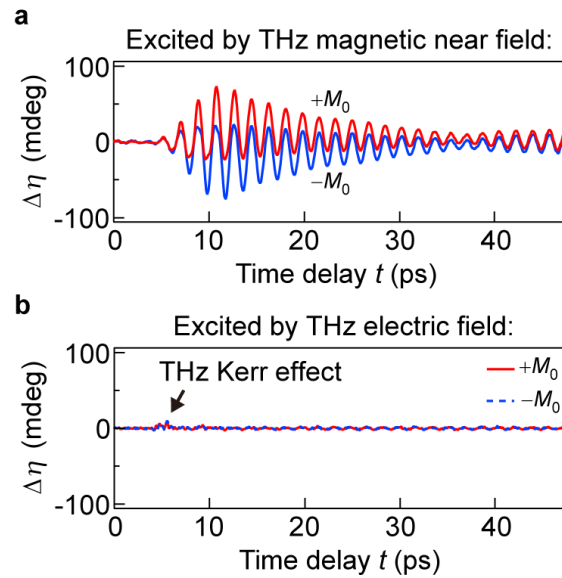


Figure 4-16. Comparison of $\Delta\eta$ between the excitations with THz near field and propagating THz pulse. The red and blue dashed curves are the ellipticity angle changes measured for initial magnetizations of $+M_0$ and $-M_0$. **a**, The experiment data is excited by the THz magnetic near field with low pass filter. **b**, The experiment data is excited by the THz pulse in free space without filter. Figure reprinted with permission from the reference⁹⁰, © 2023 Springer Nature under the terms of the Creative Commons CC BY license.

distance between the edge of the probe spot and the solenoid edge which is heated by the THz current is about 1 μm . Due to the small diffusivity of the iron-oxide insulators^{100–102}, it takes tens nanoseconds for the propagation of Joule heat from the solenoid to the probe spot.

4.9 Summary

In this work, owing to the strong excitation with the THz magnetic near field, we observed the third-order harmonic of q-AFM mode for the first time. The observations of the frequency redshift and the third-order harmonic manifest the anharmonicity of the potential energy of the q-AFM mode, $W_{\text{AFM}} = (1/2)\omega_{\text{AFM}}^2 \sin^2 \varphi$. The asymmetric amplitude (DC component) and the second-order harmonic are attributed to the nonlinearities of the magneto-optic effect related to the q-AFM mode. All these phenomena indicate that the q-AFM mode is strongly excited where the vector $\mathbf{L}$ oscillates with a large amplitude in the potential energy. The max deflection angle of $\mathbf{L}$, φ_{max} , is estimated to be 34 degrees, but the distance between two potential minima is 180 degrees, indicating that the realization of spin switching is still far from being achieved. The reason is that the barrier between the two minima is too large in the q-AFM-mode potential energy.

Driving antiferromagnetic vector $\mathbf{L}$ out of the equilibrium with a large amplitude provides a potential method for the field of spin pumping^{103–105}, where the oscillation of vector $\mathbf{L}$ in an antiferromagnet is converted to the spin current flowing into the adjacent heavy-metal layer, which is considered very important for future applications of ultrafast spintronics. Investigation of third-order (and higher-order) harmonic of spin dynamics shows a potential that the spintronics operating in THz range can be controlled with the input signal in GHz range¹⁰⁶, and also provides a new method for spin-wave computing which has so far been realized based on the simple interference¹⁰⁷. Beyond enhancing our understanding of spin nonlinearity and the potential applications of antiferromagnets, our achievements suggest that our method could serve as a

tool to control the functional properties of solids — such as ferrimagnets, multiferroelectric materials, and quantum spin systems^{108–110} — using strong THz magnetic near fields.

Chapter 5 Spin switching driven by THz-field-modified potential energy

In this chapter, we show that the switching of the magnetic order parameter can be driven by the THz magnetic-field pulse. The experiment is performed in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ near room temperature, the ellipticity angle change of the probe pulse exhibits an oscillation due to the q-FM mode, and at higher THz magnetic fields, a large and long-lived offset appears after the first half q-FM-mode cycle. This indicates that the magnetic order parameter is first driven away from the barrier between the two potential minima, and then in the subsequent motion, the magnetic order parameter move towards and crosses the barrier. Our analysis indicates that a strong and multicycle magnetic-field pulse dynamically constructs an effective potential of the magnetic system and causes spin switching. Section 5.1 provides a background on ultrafast control of q-FM mode and outlines the purpose of this chapter. Section 5.2 introduces the properties of the samples and describes the experimental setup utilized in this study. Section 5.3 presents the observed spin dynamics under weak excitation, along with the phenomena of spin switching observed under strong excitation. Section 5.4 elucidates the experimental findings, employing the sine-Gordon equation which is derived from the LLG equations to interpret the results. In Section 5.5, the relationship between the observed phenomena and Floquet engineering is explored and discussed. In section 5.6, we discussed the excitation frequency of the q-FM mode, the dependence of q-FM mode and spin switching on bias magnetic field, the phenomenon induced by THz electric near field, the dynamics of magnetic order parameters along three axes, back switching driven by stronger THz magnetic field and the influence of the frequency of the THz magnetic field on spin dynamics. Finally, we have a summary in the section 5.7.

5.1 Background

In contrast to the potential energy of q-AFM mode, the potential energy of

the q-FM mode can be modified by temperature. Thus, the barrier between two potential minima can be adjusted low enough to enable the coherent light-induced spin switching. Various methods using optical pulses in the range from NIR to MIR frequencies have been investigated for the excitation of coherent spin switching. It has been demonstrated by using IFE to generate an effective magnetic field with a NIR pulse²³ or by driving the phonon with a MIR light pulse to modify the anisotropy exchange interaction²⁷. However, heating effects cannot be avoided with these methods because they excite electrons or phonons even without intention. Manipulating spins by using THz pulses has been considered as a means of spin switching that, because of its low photon energy, does not involve strongly exciting electrons or phonons.

The spin switching in the potential energy of q-FM mode naturally requires the excitation of q-FM mode^{23,27,33}. Because when the barrier is low enough the q-FM mode is at tens GHz, it is impossible for THz pulses to resonantly excite the q-FM mode. Therefore, exploring new excitation methods using THz pulses are necessary. It has been shown that the coherent q-FM mode and spin switching can be triggered by exciting the electronic orbital transitions between crystal-field-split ground states with the electric component of THz pulses³³. This method is limited by two points: firstly, the material should have electronic orbital transitions at THz frequencies; secondly, the temperature should be low enough to suppress the thermal population of the crystal-field-split ground states, because the thermal population hinders the THz excitation. For experiments in various materials and temperature ranges, the research about excitation using THz magnetic fields is essential but has not been explored.

To advance THz-based spin-switching techniques, it seems that we must search for new methods that can be used for nonlinear manipulation of material properties. Floquet engineering is such a method^{111–114}, and it has been intensively studied in relation to electron systems^{8,9,115,116}. Recent theoretical work has showed that a classical system driven by a time-periodic external field exhibits dynamically stabilized states^{117–120} like those of quantum systems. In solid-state spin systems with long-range ordering (e.g. antiferromagnets), the

collective degrees of freedom can be regarded as a classical system. In analogy as an electron system irradiated by a time-periodic laser electric field and an inverted pendulum applied by a time-periodic mechanical force, it is reasonable to predict that the potential energy of the magnetic order parameter can be dynamically modified by a time-period magnetic field¹²¹.

So far, however, the lack of sufficiently strong and multicycle magnetic pulses has hampered such researches. Here, we studied nonlinear control of the magnetic order parameter of the canted antiferromagnet $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ near room temperature by using Tesla-class multicycle THz magnetic fields. We observed spin switching after the first half cycle of the q-FM mode oscillation and found that this phenomenon can be interpreted in terms of the dynamical modification of the potential energy of the q-FM mode induced by the strong multicycle THz magnetic fields.

5.2 Sample and experiment setup

5.2.1 Sample fabrication and properties

The single crystal $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ which is fabricated using the Floating zone method¹²² is provided by Dr. Nakajima from Osaka University and Dr. Kurihara from Tokyo University. We fabricated SARs with a thickness of 200 nm (5-nm adhesive Cr layer and a 195-nm Au layer) on the crystal surface by an electron-beam lithographic process at Nanotechnology Hub of Kyoto University. The detail of the fabrication method can be found in section 4.2.

At room temperature, the two magnetizations $\mathbf{m}_i$ ($i = 1, 2$) of the iron sublattices in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ are mainly antiferromagnetically aligned along c axis (with a slight canting angle $\beta_0 \sim 0.6^\circ$ due to DMI) and exhibit a spontaneous magnetization $\mathbf{M} = (\mathbf{m}_1 + \mathbf{m}_2)/2$ along a axis. In this material, SRT occurs in the temperature range from $T_L = 310$ K to $T_H = 330$ K as shown in Fig. 5-1, where T_L and T_H are referred to as the lower and higher critical temperatures of SRT, respectively²⁶. For temperatures $T < T_L$, $L(\mathbf{M})$ is

parallel to c axis (a axis), and for $T_H < T$, $\mathbf{L}$ ($\mathbf{M}$) is parallel to a axis (c axis). The rotation of $\mathbf{L}$ ($\mathbf{M}$) from one axis to the other in the temperature range $T_L \leq T \leq T_H$ occurs in a - c plane. This SRT process can be described by a change in the potential energy of q-FM mode with T . In the absence of the bias magnetic field, the potential energy has the following normalized form^{32,33,46}:

$$W = \frac{ab}{2} \sin^2 \theta + \frac{a}{4} \sin^4 \theta, \quad (5-1)$$

$$a = \frac{4K_2\gamma^2 H_E}{M_{Fe}}, \quad b = \frac{T - T_H}{T_H - T_L}, \quad (5-2)$$

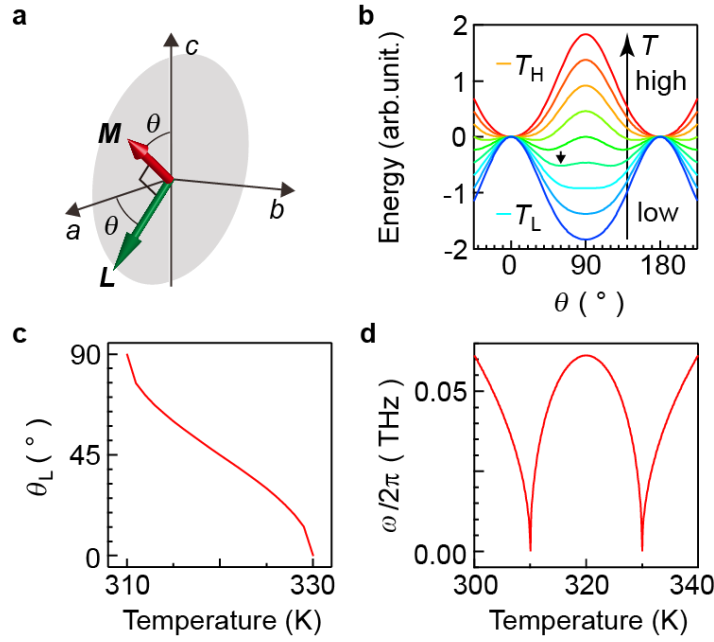


Figure 5-1. Schematic of spin reorientation transition. **a**, The orientation of $\mathbf{M}$ and $\mathbf{L}$. **b**, The potential energy varying with temperature. The arrow above the green curve indicates the left potential minimum. **c**, The temperature dependence of the angle of the left potential minimum. **d**, The temperature dependence of the frequency of the q-FM mode (curvature of the anisotropy potential).

where γ is the gyromagnetic ratio, H_E is the antiferromagnetic exchange interaction, M_{Fe} is the magnetization of one Fe^{3+} sublattice, K_2 is the temperature-independent anisotropic exchange interaction between the iron and rare earth ions. The variable θ is the angle between $\mathbf{L}$ and a axis, which is equal to the angle between $\mathbf{M}$ and c axis as shown in Fig. 5-1a. The angular positions of the two potential minima around $\theta = 90^\circ$ in the temperature range $T_L \leq T \leq T_H$ are given by $\theta_L = \arcsin \sqrt{-b}$ and $\theta_R = \pi - \arcsin \sqrt{-b}$. The potential energy is shown in Fig. 5-1b. We found that as temperature increases approaching T_L , the curvature of potential minimum at 90° becomes small. When temperature increases beyond T_L , potential minimum at 90° splits and the curvatures increase. Then, the potential minima broaden and the barrier increases with increase of temperature. When approaching T_H , the potential minima arrive $\pm 180^\circ$ and the curvatures decrease again. Finally, as temperature continues to increase, the curvatures at $\pm 180^\circ$ increase. The position of the left potential minimum is shown in Fig. 5-1c and the curvature is shown in Fig. 5-1d. Because the oscillation of θ corresponds to the q-FM mode (the swing motion of $\mathbf{M}$ and $\mathbf{L}$ in a - c plane), the curvature indicates the frequency of q-FM mode, $\omega_{\text{FM}} = \sqrt{d^2W/d\theta^2}$. As shown in Fig. 5-1d, the frequency of q-FM mode becomes zero at T_L and T_H . Therefore, the frequency of q-FM mode functions as the indicator of the phase-transition temperature.

5.2.2 Experiment setup

Because the efficiency of THz generation becomes saturated when the pump pulse energy reaches 3 mJ, to obtain stronger THz pulses, we superpose two THz pulses generated from single LiNbO₃ crystal with a finite time interval. The laser output with pulse energy 7 mJ is first divided into two NIR (800 nm) beams by using a beam splitter. The weaker NIR beam with 1% of the total output power is used to probe the sample response. A delay stage is used to control the delay time between the weak NIR beam and the strong NIR beam. The stronger NIR beam is further divided into two beams with equal power. Another delay stage is used to control the delay time between these two strong femtosecond laser pulses. The two pulses are used to generate two intense THz pulses in a LiNbO₃ crystal as shown in Fig. 5-2 based on the method introduced in the subsection 3.1.1. This pair of THz pulses is referred to as the THz double pulse. The THz pulses are focused on the sample by using an off-axis parabolic mirror with a focal length of 50 mm. The maximum peak electric fields of the two single-cycle THz pulses before the low-pass filter (< 0.68 THz) were 1.0 MV/cm and 0.75 MV/cm. The filter is also introduced in the subsection 3.2.4. The time delay Δt between the two strong femtosecond laser pulses for THz generation was set to 4.48 ps, which allows us to avoid saturation and a reduction in the THz generation efficiency. The generated THz magnetic near

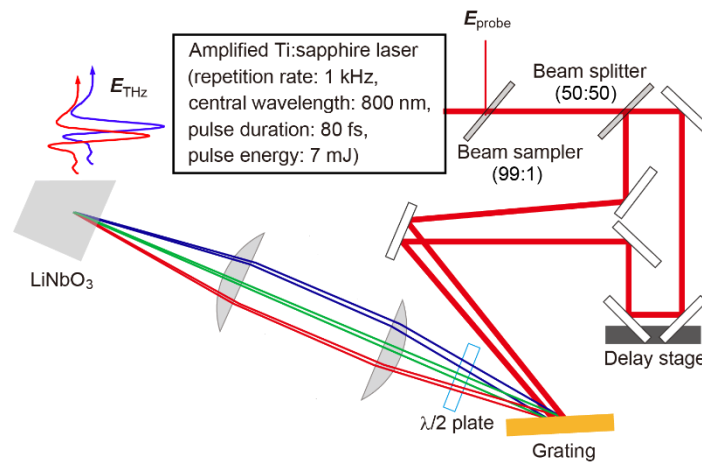


Figure 5-2. The generation of THz-double pulses. Figure reprinted with permission from the reference⁹¹.

field $B_{\text{THz}}^{\text{NF}}$ is perpendicular to the sample surface and along c -axis as shown in Fig. 5-3.

The time-resolved Faraday ellipticity measurements is introduced in the section 3.3. The polarization directions of the THz light and the probe light are parallel and along b axis. A home-made coil heater was used to increase the sample temperature. During our pump–probe experiments, the sample was in a bias magnetic field B_{DC} of about 2 mT to prepare an initial state where $\mathbf{L}$ ($\mathbf{M}$) is oriented at the angle θ_L (θ_R). The thermal fluctuation may create a few magnetic domains in which $\mathbf{L}$ is at θ_R , because the temperature of experiment is around the critical point T_L where the potential barrier is small. However, the experiment signals at different positions show the same behavior. Thus, it is reasonable to consider that the experiment signal is an average over different domains where the domain size is much smaller than the spot size of the probe pulse (diameter: 1.2 μm).

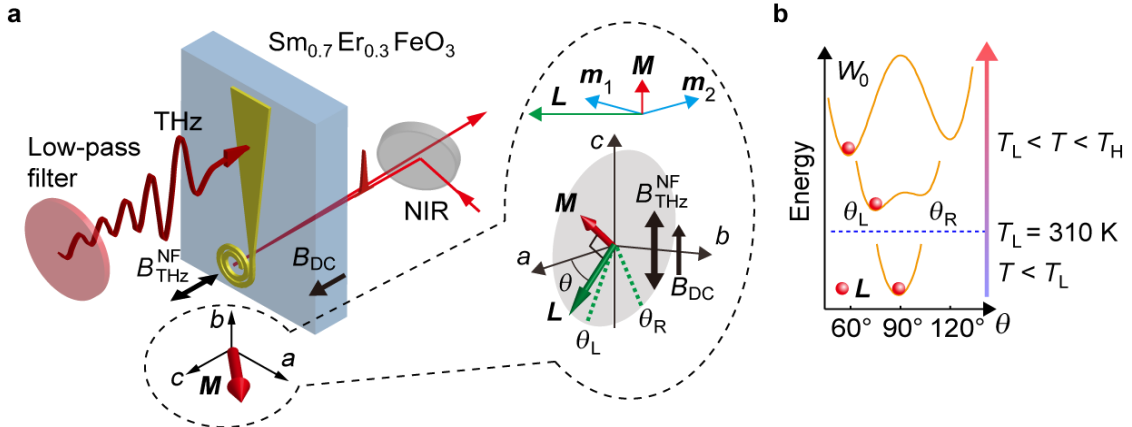


Figure 5-3. **a**, Schematic diagram of the experiment. A SAR was fabricated on a 70- μm -thick $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$ single crystal to generate a strong THz magnetic field $B_{\text{THz}}^{\text{NF}}$ along c axis. The orientation of $\mathbf{M}$ and $\mathbf{L}$ in a – c plane defined by θ is shown in the inset. The grey area indicates a – c plane. **b**, The temperature dependence of potential energy. Figure reprinted with permission from the reference⁹¹.

5.3 Experimental result

5.3.1 Excitation by relatively weak THz magnetic pulse

We investigated the sample response at the beginning by using a moderate excitation where a single THz pulse is applied to the SAR. The measured temporal development of $\Delta\eta$ is given by the coloured curves Fig. 5-4a for four different temperatures. The time moment of THz pulse arriving sample is set at 0 ps by hand in this chapter 5. The difference of these time moments in chapter 4 and chapter 5 comes from the manual setting, and does not indicate that between the two experiments, there is a time delay of THz pulse arriving sample. These curves exhibit a superposition of fast and slow oscillations. Fig. 5-4b shows the Fourier spectrum of the $\Delta\eta$ curve for $T = 315$ K where a fast oscillation is marked at about 0.545 THz, which is in the frequency range of

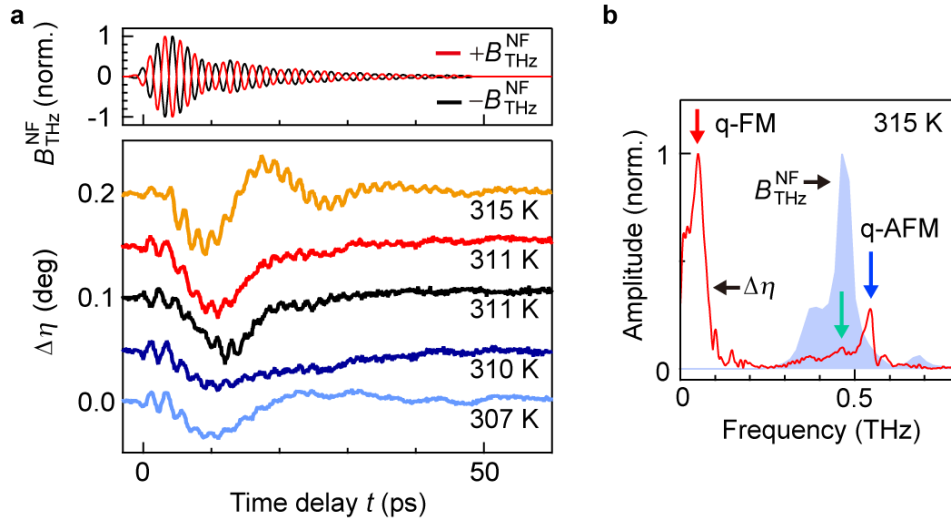


Figure 5-4. THz-pump-induced ellipticity-angle change $\Delta\eta$ as a function of temperature. **a**, Upper panel: the red curve shows the temporal evolution of $B_{\text{THz}}^{\text{NF}}$ along c axis, and the black curve shows the inverse pulse waveform ($-B_{\text{THz}}^{\text{NF}}$) obtained by rotating the SAR by 180° about c axis. Lower panel: ellipticity-angle change $\Delta\eta$ as a function of the pump-probe time delay for four temperatures. The curves are offset for clarity. **b**, The red curve and the blue shaded area are the spectra of $\Delta\eta$ at 315 K and $B_{\text{THz}}^{\text{NF}}$, respectively. The red, green and blue arrows indicate the q-FM mode at about 0.05 THz, the fast oscillation that follows $B_{\text{THz}}^{\text{NF}}$ (which has a peak at 0.46 THz), and the q-AFM mode at 0.545 THz, respectively. Figure reprinted with permission from the reference⁹¹.

the THz magnetic-field pulse. This oscillation peak is attributed to the q-AFM mode. Besides, another fast oscillation component indicated by the green arrow in Fig. 5-4b is the forced oscillation which oscillates at the frequency of the THz magnetic near field. On the other hand, the slow oscillation at about 0.05 THz (red arrow) lies clearly out of the spectral range of THz magnetic near field $B_{\text{THz}}^{\text{NF}}$, which indicates a strongly non-resonant character of the excitation process. This oscillation peak is attributed to the q-FM mode. The q-FM and q-AFM modes are discussed in the following detailly.

The softening shown in Fig. 5-5a verifies that the slow oscillation is due to the q-FM mode. The temperature 310 K where the frequency is lowest defines T_L . We investigated the dependence of the q-FM mode amplitude on the peak amplitude of THz magnetic near field $B_{\text{amp}}^{\text{NF}}$: As shown in Fig. 5-5b, the q-FM mode amplitude exhibits a quadratic dependence on $B_{\text{amp}}^{\text{NF}}$, which is clearly different from the linear dependence that would be expected for resonant excitation. The black curve in Fig. 5-4a was obtained using a THz magnetic near field with an inverse waveform (“ $-B_{\text{THz}}$ ” in the upper panel) and clarifies that the sign of the q-FM mode oscillation is not affected by the sign of $B_{\text{THz}}^{\text{NF}}$. These behaviors cannot be explained by the resonant excitation.

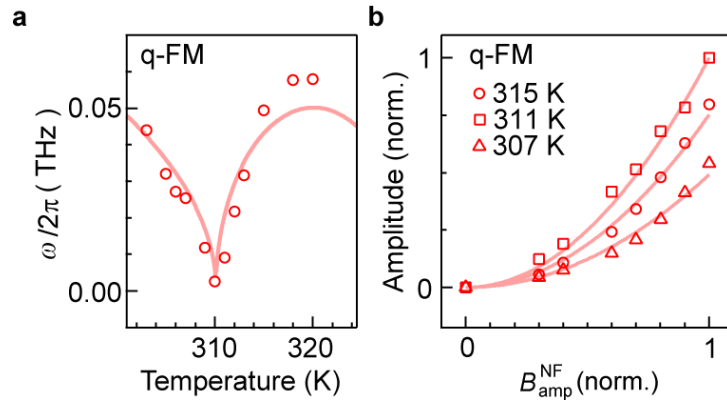


Figure 5-5. a, The temperature dependences of q-FM frequency (upper panel). The red curves are guides to the eye. **b**, The dependence of the q-FM mode amplitude on the magnetic-field peak amplitude $B_{\text{amp}}^{\text{NF}}$ for three temperatures. The solid lines are proportional to the square of $B_{\text{amp}}^{\text{NF}}$. Figure reprinted with permission from the reference⁹¹.

The frequency of the q-AFM mode is not sensitive to temperature as shown in the upper panel of Fig. 5-6a. The linear increase of the q-AFM-mode amplitude for $T > T_L$ is shown in the lower panel of Fig. 5-6a. It is explained as follows: For $T > T_L$, the observed q-AFM mode amplitude should be proportional to $\cos^2\theta_L$. The Zeeman torque for the excitation of q-AFM mode is proportional to the projection of $B_{\text{THz}}^{\text{NF}}$ onto $\mathbf{M}$ (leading to the factor $\cos\theta_L$), and $\Delta\eta$ is proportional to the projection of the radial change of $\mathbf{M}(\mathbf{L})$ onto $c(a)$ axis (leading to another $\cos\theta_L$). Finally, the relation $\cos^2\theta_L = 1 - (T_H - T)/(T_L - T_H)$ leads to the linear dependence on the temperature. These facts verify the oscillation is due to the q-AFM mode. The linear dependence on $B_{\text{amp}}^{\text{NF}}$ shown in Fig. 5-6b verifies that the resonant nature of the excitation.

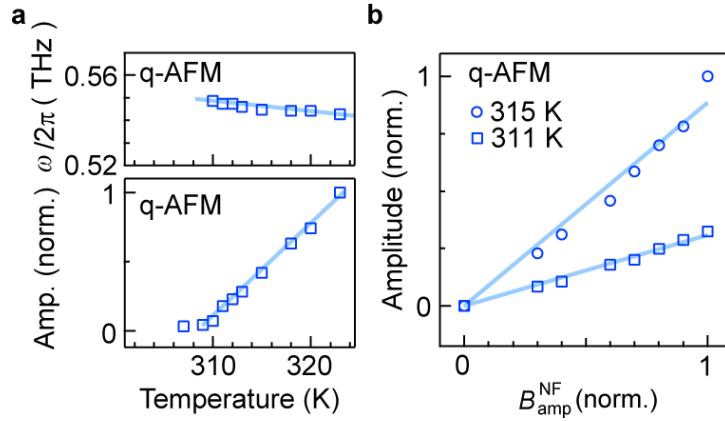


Figure 5-6 a, The temperature dependences of q-AFM frequency (upper panel) and q-AFM amplitude (lower panel). The blue curves are guides to the eye. **b**, The dependence of the q-AFM mode amplitude on the magnetic-field peak amplitude $B_{\text{amp}}^{\text{NF}}$ for two temperatures. The solid lines are proportional to $B_{\text{amp}}^{\text{NF}}$. Figure reprinted with permission from the reference⁹¹.

5.3.2 Spin switching driven by strong THz magnetic pulse

When the excitation is relatively weak (Fig. 5-4), $\mathbf{L}$ and $\mathbf{M}$ always relax to the initial potential minimum θ_L in the double-well potential. To induce spin switching, we used a stronger THz magnetic near field, and to avoid that the THz generation reaches the saturation regime, we used a superposition of two THz pump pulses. When the THz-double pulses are applied with full power,

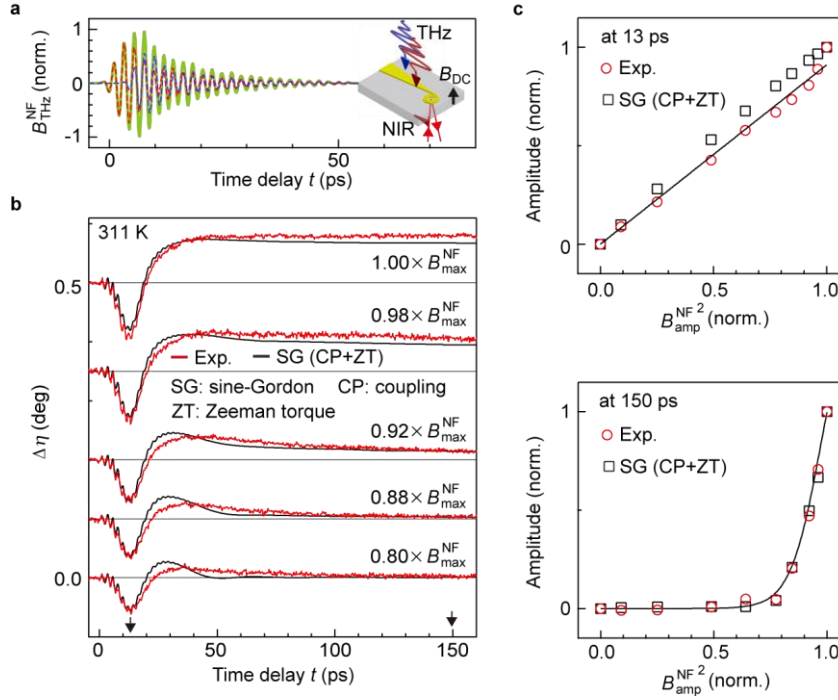


Figure 5-7. **a**, The time trace of the strong multicycle THz magnetic field (green curve) generated by irradiating the SAR with two THz pulses (red and blue curves) separated by a time interval of $\Delta t = 4.48$ ps. **b**, The experimental data of $\Delta\eta$ at 311 K for different magnetic-field amplitudes $B_{\text{amp}}^{\text{NF}}$ are shown by the red curves. The black curves show the predictions for $\Delta\cos\theta = \cos\theta - \cos\theta_L$ based on the sine-Gordon equation including fluctuations. The results are offset for clarity. The two black arrows at the bottom of the figure indicate the time delays of 13 ps and 150 ps. **c**, The amplitudes of the experimental and theoretical data in **b** at 13 ps as a function of $B_{\text{amp}}^{\text{NF}^2}$ (upper panel) and those at 150 ps as a function of $B_{\text{amp}}^{\text{NF}^2}$ (lower panel). The red open circles and black open squares represent the experimental results and the results predicted by the sine-Gordon equation including fluctuations, respectively. The max amplitude of THz magnetic near field $B_{\text{max}}^{\text{NF}}$ used in the sine-Gordon equations is 1.45 T. This value is 41% of 3.53 T which is calculated by FDTD simulation using the practical incident THz electric pulse with max power. Figure reprinted with permission from the reference⁹¹.

the max value of peak amplitude $B_{\text{amp}}^{\text{NF}}$ can be achieved and is indicated by $B_{\text{max}}^{\text{NF}}$.

Figure 5-7 shows the sample response with different values of $B_{\text{amp}}^{\text{NF}}$ at $T = 311$ K, where the potential barrier between the minimum at θ_L and that at θ_R is relatively small. In the range $t > 20$ ps, a large offset towards positive $\Delta\eta$ value emerges as $B_{\text{amp}}^{\text{NF}}$ is increased. As shown in Fig. 5-7b, the offset at about 150 ps steeply grows after $B_{\text{amp}}^{\text{NF}}$ exceeds a critical value.

To characterize the dependence of the q-FM mode amplitude on $B_{\text{amp}}^{\text{NF}}$, we plot the experimental values of $\Delta\eta$ at 13 ps versus $B_{\text{amp}}^{\text{NF}^2}$ in the upper panel of Fig. 5-7c. The quadratic dependence on $B_{\text{amp}}^{\text{NF}}$ is evidence of a nonlinear excitation process. To evaluate the threshold behavior of the offset at $t > 20$ ps quantitatively, the experimental values of $\Delta\eta$ at 150 ps are plotted in the bottom panel of Fig. 5-7c. The obtained result is obviously steeper than that of the q-FM mode amplitude at 13 ps. Furthermore, as temperature is varied, the offset at $t > 20$ ps changes drastically (Fig. 5-8), indicating that this offset only appears when the barrier at $\theta = 90^\circ$ is small enough.

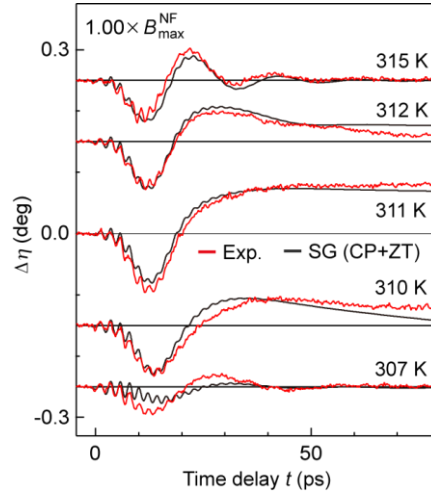


Figure 5-8. The time traces of $\Delta\eta$ obtained at different temperatures in the range from 307 to 315 K using the strong multicycle THz magnetic field. The black curves show the predictions for $\Delta\cos\theta = \cos\theta - \cos\theta_L$ based on the sine-Gordon equation including fluctuations. The curves are offset for clarity. Figure reprinted with permission from the reference⁹¹.

The existence of critical value of $B_{\text{amp}}^{\text{NF}}$ as well as the drastic temperature dependence are the clear evidences that $\mathbf{L}$ and $\mathbf{M}$ overcome the barrier and move into the second potential minimum. The spins switched by the THz magnetic near field relax to the initial potential minimum before the next pump pulse arrives (after 1 ms). Besides, according to the other study where similar spin switching was achieved using the laser source with the repetition rate of 3 kHz³³, I can speculate that the lifetime of the switched state (offset) is less than 0.3 ms. The spins are switched back to the initial potential minimum not only due to thermal fluctuation¹²³, but also because the exchange interaction with spins outside the newly created domain assists in switching the spins inside the domain back. The excess energy when spins are switched back to the initial potential minimum is finally transferred to acoustic phonon through various ways such as four-magnon scattering⁴⁵ and magnon-phonon interaction¹²⁴.

Spin switching results in a final orientation of $\mathbf{L}$ and $\mathbf{M}$ that is different from the initial orientation, and thus provides information about the physical meaning of the “downward” in the range $t < 20$ ps. We have shown in section 4.6, the observable $\Delta\eta$ is determined by an odd function of $\Delta L_a(\Delta M_c)$. The opposite sign of $\Delta\eta$ reflects the different direction of motion of $\Delta L_a(\Delta M_c)$. Therefore, the observed switching process ($\Delta\eta > 0$) clarifies that the initial “downward” movement ($\Delta\eta < 0$) corresponds to the motion of $\mathbf{L}$ away from the barrier at 90° .

With this information, we can analyse the details of the observed switching by dividing the $\Delta\eta$ curve into three regions as shown in Fig. 5-9. The magnetic near field is shown in grey for comparison. Before pumping, $\mathbf{L}$ has an orientation according to the equilibrium condition ($\theta = \theta_L$). When the system is exposed to the strong THz magnetic field, $\mathbf{L}$ is driven from the initial minimum to the $+a$ direction (process 1 in Fig. 5-9; the rotation of $\mathbf{L}$ indicated by the orange arrow leading to $\theta < \theta_L$), which results in the “downward” movement of $\Delta\eta$. After the envelope of the THz magnetic field has decayed sufficiently, $\mathbf{L}$ starts to move back to the original minimum, and as a result of “inertia”, it will pass the minimum at θ_L and proceed towards the barrier at $\theta = 90^\circ$ (process

2; $\mathbf{L}$ behaves according to the law of inertia²³ due to the coupling between the sublattice spins). If the initial driving process is strong enough, $\mathbf{L}$ can overcome the barrier and then, through dissipation, it relaxes to the minimum at θ_R (process 3). This leads to the observed large positive offset in $\Delta\eta$.

We emphasize that process 1 describes a rather unexpected phenomenon: $\mathbf{L}$ is initially driven away from the barrier (θ becomes less than θ_L). This peculiar initial motion is in stark contrast to the results of previous investigations that used optical pulses or THz electric pulses to trigger spin switching^{23,27,33}; in all previous reports, $\mathbf{L}$ was initially driven towards the barrier. In other words, the signs of $\Delta\eta$ at the initial and final stages of the switching process were the same.

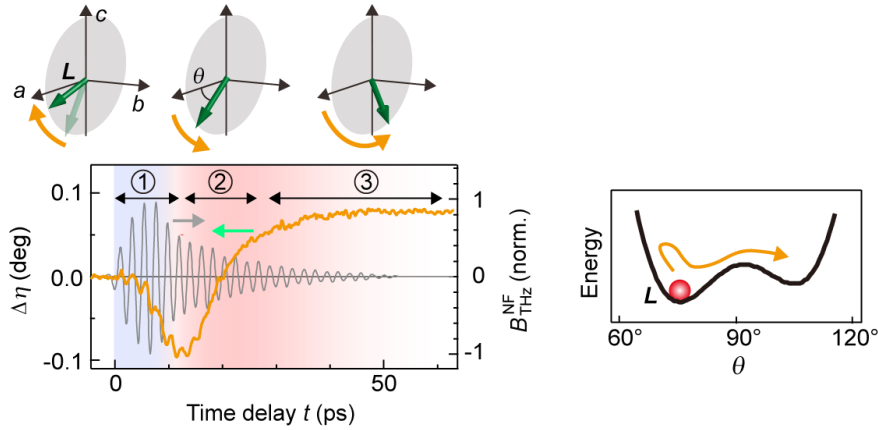


Figure 5-9. The schematic of the spin switching. The spin switching is divided into three-time ranges, and the motion of $\mathbf{L}$ in each range is illustrated above the curve. The motion of $\mathbf{L}$ in the potential energy is shown in the right panel. Figure reprinted with permission from the reference⁹¹.

5.4 Theory based on LLG equations

To investigate what leads to the initial slow motion of $\mathbf{L}$ away from the barrier, we derived the sine-Gordon equation from the two-sublattice LLG equations, and then rewrote the sine-Gordon equation by using effective potential. The consistent results of direct solution and the solution with the effective-potential approximation indicate, that the potential of the system is dynamically modified by the multicycle THz magnetic near field. This mechanism is similar as Floquet engineering which is often studied in the electron systems.

5.4.1 Derivation of the sine-Gordon equation

The result of LLG equations Eq. (2-20) is used here,

$$\begin{aligned} \dot{\mathbf{L}} \times \mathbf{H}_D + \dot{\mathbf{B}} - \dot{\mathbf{L}}(\mathbf{B} \cdot \mathbf{L}) - \mathbf{L}(\dot{\mathbf{B}} \cdot \mathbf{L} + \mathbf{B} \cdot \dot{\mathbf{L}}) + \frac{\dot{\mathbf{L}} \times \mathbf{L}}{\gamma} = \\ -\gamma(\mathbf{L} \times \mathbf{H}_D) \times \mathbf{B} + \gamma(\mathbf{B} \cdot \mathbf{L})\mathbf{L} \times \mathbf{B} \\ -(\dot{\mathbf{L}} \times \mathbf{L}) \times \mathbf{B} + 2H_E\gamma\mathbf{L} \times \frac{\partial V}{\partial \mathbf{L}}, \end{aligned} \quad (5-3)$$

$$\begin{aligned} V = H_E \mathbf{M}^2 - \mathbf{M} \cdot (\mathbf{L} \times \mathbf{H}_D + \mathbf{B}) \\ -A_{aa}L_a^2 - A_{cc}L_c^2 + A_4(L_a^4 + L_b^4 + L_c^4), \end{aligned} \quad (5-4)$$

where $\mathbf{H}_D$ is the Dzyaloshinskii–Moriya interaction oriented at b axis. A_{aa} , A_{cc} and A_4 are anisotropic interactions which characterize SRT. A_{cc} depends on temperature. We describe $\mathbf{L}$ by using sphere coordinates as shown in Fig. 5-10, $\mathbf{L} = L(\cos\theta\cos\varphi, \cos\theta\sin\varphi, -\sin\theta)$. We define $L = 1$. Because the q-FM mode is the motion of $\mathbf{L}$ in a – c plane, the b -axis component of Eq. (5-3) characterizes the q-FM mode, and is given by,

$$\begin{aligned} \ddot{\theta} + c\dot{\theta} = & -\chi(B_{DC} + B_{THz}^{NF}(t))\sin\theta \\ & -a\sin\theta\cos\theta(\sin^2\theta + b) \\ & +2\gamma B_{THz}^{NF}(t)\dot{\phi}\cos\theta\sin\theta + \gamma\dot{B}_{THz}^{NF}(t)\phi\cos\theta\sin\theta, \end{aligned} \quad (5-5)$$

$$a = 4H_E\gamma^2(4A_4), b = \frac{(A_{aa}-A_{cc}-2A_4)}{4A_4}, \chi = \gamma^2 H_D, \quad (5-6)$$

where the small terms are ignored, such as $\ddot{\phi}\sin\phi$, $\dot{\phi}^2$, $\dot{\theta}\dot{\phi}$ and $\dot{\theta}\sin\phi$. The damping factor is added later according to the literature³², $c = 2\gamma H_E\alpha_{LLG}$. α_{LLG} is the Gilbert damping which is attributed to the four-magnon scattering⁹⁷, as well as the magnon-phonon interaction¹²⁴. This is the sine-Gordon equation with respect to θ considering the coupling to the q-AFM mode which is depicted by ϕ . On the right-hand side, the first term is the Zeeman torque of the external magnetic field including the bias magnetic field B_{DC} and THz magnetic near field $B_{THz}^{NF}(t)$. The second term is the torque due to anisotropy interaction. The third and fourth terms are the torques due to coupling¹²⁵. The parameters a and b describing the anisotropy interaction are equivalent with those by using the critical temperature of phase transition,

$$a = \frac{4K_2\gamma^2 H_E}{M_{Fe}}, b = \frac{T-T_H}{T_H-T_L}. \quad (5-7)$$

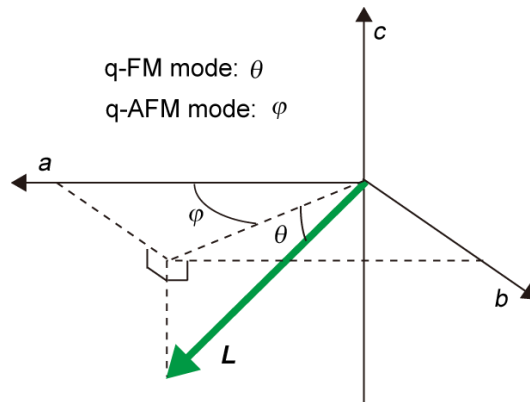


Figure 5-10. The definition of the sphere coordinates of $\mathbf{L}$. At equilibrium state, ϕ is equal to zero, and θ is determined by the anisotropy interactions. Figure reprinted with permission from the reference⁹¹.

Because the q-AFM mode is the swing motion of $\mathbf{L}$ perpendicular to a - c plane, it is described by the a -axis and c -axis components of Eq. (5-3). The two components are added together,

$$\begin{aligned} \ddot{\phi}\cos\theta + c\dot{\phi}\cos\theta = \\ -\omega_{\text{AFM}}^2\phi\cos\theta + \gamma\dot{B}_{\text{THz}}^{\text{NF}}(t)\cos\theta - 2\gamma B_{\text{THz}}^{\text{NF}}(t)\dot{\theta}\sin\theta, \end{aligned} \quad (5-8)$$

$$\begin{aligned} \omega_{\text{AFM}}^2 = \gamma^2 H_{\text{D}}^2 + \gamma^2 H_{\text{D}} B_{\text{DC}} \cos\theta - \gamma^2 B_{\text{DC}}^2 \sin^2\theta \\ + 4H_{\text{E}}\gamma^2 (A_{aa}\cos^2\theta + A_{cc}\sin^2\theta) \\ - 8H_{\text{E}}\gamma^2 A_4 (\sin^4\theta + \cos^4\theta), \end{aligned} \quad (5-9)$$

where the small terms are ignored, such as $\ddot{\theta}\sin\phi$, $\dot{\phi}^2\sin\phi$, $\dot{\theta}\dot{\phi}$ and $\dot{\theta}\sin\phi$. The damping factor $c = 2\gamma H_{\text{E}}\alpha_{\text{LLG}}$ is added later. The first term on the right-hand side of Eq. (5-8) indicates the intrinsic frequency of the q-AFM mode determined by the various exchange interactions. The second and third terms are the Zeeman torque of THz magnetic near field and the coupling to q-FM mode, respectively.

We numerically solved the Eq. (5-8) by ignoring the coupling term and then employed the results to numerically solve the Eq. (5-5). It is reasonable to ignore the coupling term in Eq. (5-8) because it is very small. The values of the parameters are shown in Table 5-1 which are taken from the previous studies, and are adjusted by fitting the frequencies of the q-AFM and q-FM modes. We compared the numerical solutions of the LLG equations Eqs. (2-3) – (2-5), with the sine-Gordon equation Eq. (5-5). We found that they lead to very similar results as shown in Fig. 5-11. It confirms that the Eqs. (5-5) and (5-8) are correct.

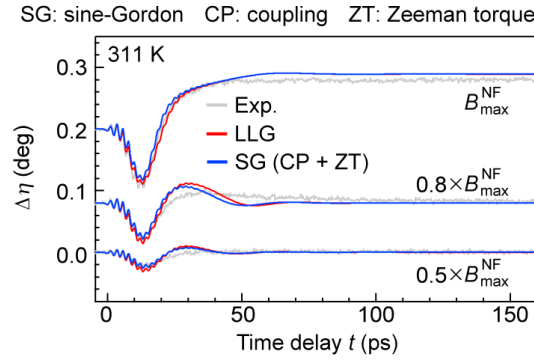


Figure 5-11. The experimental results $\Delta\eta$, calculational results $\Delta\cos\theta$ using the LLG equations and the sine-Gordon equation. To compare with experimental results, all calculation results are scaled by the same factor. Figure reprinted with permission from the reference⁹¹.

Table 5-1| The parameters used in the calculations of the two-sublattice LLG equations Eqs. (2-3) – (2-5) and the sine-Gordon equation Eq. (5-5).

Parameter	Value ^{40,45}
H_E	650 T
H_D	13.5 T
γ	1.76×10^{11} rad/(s·T)
α_{LLG}	0.675×10^{-3}
A_{aa}	76×10^{-3} T
$A_{cc}(311K)$	77.6×10^{-3} T
A_4	91.7×10^{-5} T

5.4.2 Numerical calculation of sine-Gordon equation

To verify that the q-FM mode and the spin switching can be described by the sine-Gordon equation, Eqs. (5-5) and (5-8) is numerically calculated. After calculation, we obtain temporal development of θ (q-FM mode) and φ (q-AFM mode). We can use the calculation results $\Delta\cos\theta$ to explain the motion of q-FM mode exhibited by experimental results $\Delta\eta$ (detail is discussed in the section 5.6.4).

We find that the experimental results Figs. 5-7 and 5-8 can be reproduced by the numerical calculation based on the sine-Gordon equation Eq. (5-5) including fluctuations as shown by the black curves (the influence of thermal fluctuations and magnetization domains are explained in Appendix A1).

The max amplitude of THz magnetic near field $B_{\max}^{\text{NF}}$ used in the LLG and sine-Gordon equations is 1.45 T. This value is 41% of 3.53 T which is calculated by FDTD simulation using the practical incident THz electric pulse with max power. The possible reason of the difference is considered that the gold deposited on the sample surface may have imperfections thus leading to a relatively low conductivity.

Then, we investigated the strength ratio between the Zeeman torque and the coupling term in Eq. (5-5). The Eq. (5-5) was numerically solved by considering either the Zeeman torque or the coupling term as shown in Fig. 5-12. The coupling term and the Zeeman torque both induce the downward slow motion at the beginning. The contributions from the two terms are shown in Fig. 5-12b where the amplitude of slow motion at 13 ps is plot, and we found that the coupling is about 4 times larger than the Zeeman torque. Besides, as shown by the amplitude at 150 ps, we found that near the threshold, the two terms are both necessary for the spin switching.

We verified that the q-FM mode and the spin switching can be described by the sine-Gordon equation. But, the physical mechanism for the peculiar motion of $\mathbf{L}$ away from the barrier at the beginning has not been uncovered.

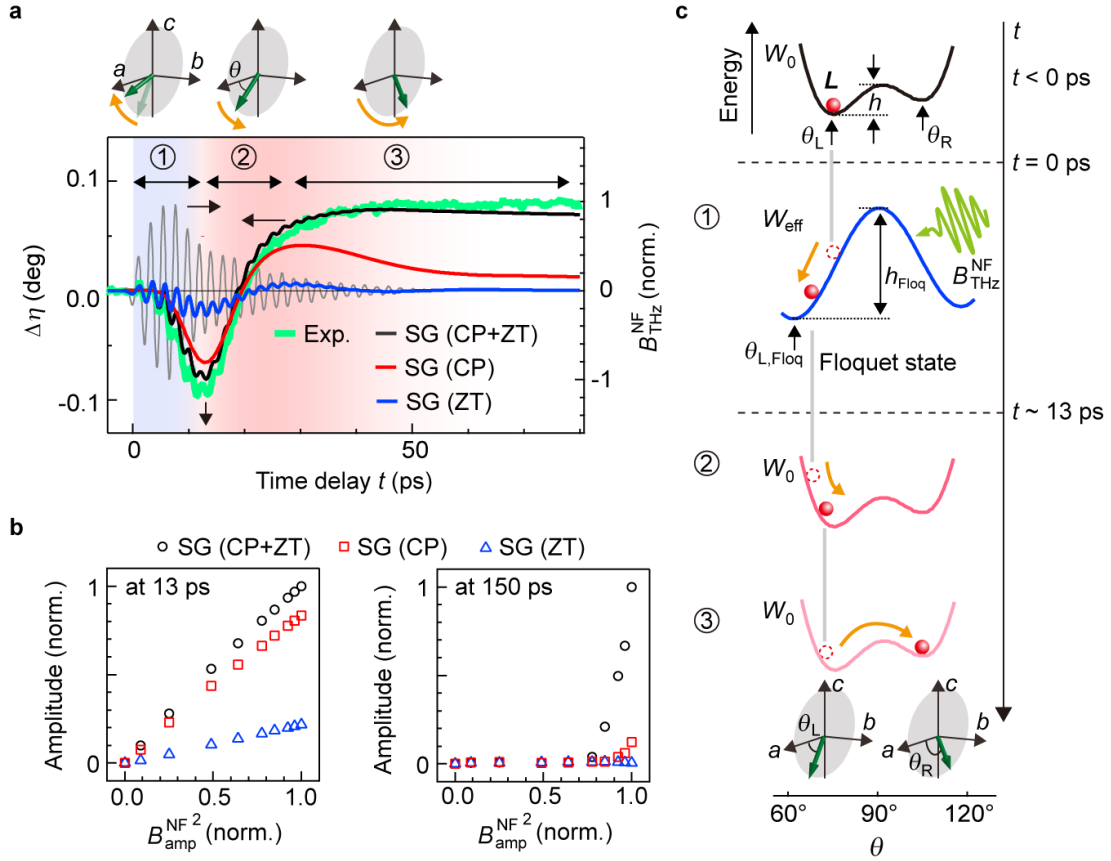


Figure 5-12. Three-step spin switching via a dynamically stabilized state. **a**, The temporal evolution of $\Delta\eta$ at 311 K is shown by the green curve, and the solution of the sine-Gordon equation is shown by the black curve. The red and blue curves show the results of calculations only considering the coupling term or the Zeeman torque, respectively. The spin switching is divided into three-time ranges, and the motion of $\mathbf{L}$ in each range is illustrated above the curve. The black vertical arrow at the bottom of the figure indicates a time delay of 13 ps. **b**, The amplitudes of the slow motion of theoretical data in **a** at 13 ps as a function of $B_{\text{amp}}^{\text{NF}^2}$ (left panel) and those at 150 ps as a function of $B_{\text{amp}}^{\text{NF}^2}$ (right panel). **c**, The variation of the potential and the motion of $\mathbf{L}$ at four conditions: before $B_{\text{THz}}^{\text{NF}}$ is applied, during the time when $B_{\text{THz}}^{\text{NF}}$ exhibits a large amplitude, soon after the peak of $B_{\text{THz}}^{\text{NF}}$, and the following spin switching. Figure reprinted with permission from the reference⁹¹.

5.4.3 The sine-Gordon equation with effective potential

To understand the peculiar motion of $\mathbf{L}$ away from the barrier at the beginning, we consider a dynamical modification of the potential energy. We analytically solved the sine-Gordon equation by replacing the potential energy interacting with the fast-oscillating magnetic field with a “time-averaged” effective potential that varies with the envelope of the field. It can be obtained in two steps.

Firstly, the effective potential energy contributed by the coupling is introduced which is obtained by transforming Eq. (5-5) to an equation including only one variable θ . To do that, the Eq. (5-8) is analytically solved. Because the amplitudes of q-FM mode in both experiment and numerical calculation obey the quadratic dependence on amplitude of THz magnetic near field, the coupling term in Eq. (5-8) can be ignored and θ can be regarded as a constant. By assuming the THz magnetic near field having a very slow-varying envelope, $B_{\text{THz}}^{\text{NF}}(t) = B_{\text{env}}^{\text{NF}}(t)\cos(\omega t)$, Eq. (5-8) is solved,

$$\varphi \cos \theta = Q_{\text{AFM}}(t) \sin(\omega t + p), \quad (5-10)$$

$$Q_{\text{AFM}}(t) = \frac{-\gamma \omega B_{\text{env}}^{\text{NF}}(t) \cos \theta}{\sqrt{(\omega_{\text{AFM}}^2 - \omega^2)^2 + (\omega c)^2}}, \quad (5-11)$$

$$p = \arccos \left(\frac{(\omega_{\text{AFM}}^2 - \omega^2)}{\sqrt{(\omega_{\text{AFM}}^2 - \omega^2)^2 + (\omega c)^2}} \right), \quad (5-12)$$

where the phase delay p is caused by finite damping. Then by inserting Eq. (5-10) into Eq. (5-5), we obtain,

$$\begin{aligned}\ddot{\theta} + c\dot{\theta} = & -\chi(B_{\text{DC}} + B_{\text{THz}}^{\text{NF}}(t))\sin\theta - \frac{a}{2}(b + \sin^2\theta)\sin 2\theta \\ & + \gamma\omega B_{\text{env}}^{\text{NF}}(t)Q_{\text{AFM}}(t)\sin\theta\left(\frac{3}{2}\cos(2\omega t + p) + \frac{1}{2}\cos p\right).\end{aligned}\quad (5-13)$$

The third term of Eq. (5-13) is the effective potential energy contributed by the coupling.

Secondly, we apply the analysis in analogy with the Kaptiza pendulum to Eq. (5-13) due to the similarity of equations. The term oscillating at 2ω can be ignored, because after applying the analysis it would become very small (and it also induces the dependence higher than the second order on THz magnetic near field, which is not observed). Eq. (5-13) is rewritten by,

$$\begin{aligned}\ddot{\theta} + c\dot{\theta} = & -\chi(B_{\text{DC}} + B_{\text{THz}}^{\text{NF}}(t))\sin\theta \\ & - \frac{a}{2}(b + \sin^2\theta)\sin(2\theta) \\ & - \Psi_{\text{CP}}B_{\text{env}}^{\text{NF}^2}(t)\sin(2\theta),\end{aligned}\quad (5-14)$$

$$\Psi_{\text{CP}} = \frac{\gamma^2\omega^2(\omega_{\text{AFM}}^2 - \omega^2)}{4((\omega_{\text{AFM}}^2 - \omega^2)^2 + (\omega c)^2)}.\quad (5-15)$$

When our THz magnetic pulse at frequency of ~ 0.46 THz is applied, the motion of θ consists of two components: a slow motion determined by the potential energy, and a fast motion that is directly related to the instantaneous THz magnetic field: In analogy with the Kapitza pendulum (Appendix A2), θ can be decomposed into a fast component and a slow component,

$$\theta = \theta_{\text{fast}} + \theta_{\text{slow}}.\quad (5-16)$$

Hereafter, we consider the relatively high-frequency regime, which is defined as the regime where $\omega \gg c$ and $\omega^2 \gg ab/2, \Psi_{\text{CP}} B_{\text{env}}^{\text{NF}^2}(t)$ holds. θ_{fast} follows the forced oscillation of the magnetic pulse, and we assume that its magnitude is small, i.e., $|\theta_{\text{fast}}| \ll 1$. On the other hand, the time scale of the motion of θ_{slow} is significantly longer than the period of the THz magnetic pulse, and therefore, the motion of θ_{slow} is affected by the average of the fast oscillation of $B_{\text{THz}}^{\text{NF}}$ and θ_{fast} . By using an expansion in powers of θ_{fast} and calculating the temporal average, we derive the following approximate equations of motion:

$$\ddot{\theta}_{\text{fast}} + c\dot{\theta}_{\text{fast}} = -\chi \sin \theta_{\text{slow}} B_{\text{env}}^{\text{NF}}(t) \cos(\omega t) + O(\theta_{\text{fast}}^2), \quad (5-17)$$

$$\begin{aligned} \ddot{\theta}_{\text{slow}} + c\dot{\theta}_{\text{slow}} = & -\chi \cos \theta_{\text{slow}} B_{\text{env}}^{\text{NF}}(t) \langle \cos(\omega t) \theta_{\text{fast}} \rangle_{\tau} \\ & + \left[\left(ab + 2\Psi_{\text{CP}} B_{\text{env}}^{\text{NF}^2}(t) \right) \sin(2\theta_{\text{slow}}) - \frac{3a}{4} \sin(4\theta_{\text{slow}}) \right. \\ & \left. + a \sin(2\theta_{\text{slow}}) \sin^2 \theta_{\text{slow}} + \chi B_{\text{DC}} \sin \theta_{\text{slow}} \right] \langle \theta_{\text{fast}}^2 \rangle_{\tau} \\ & - \chi \sin \theta_{\text{slow}} B_{\text{DC}} - \frac{a}{2} (b + \sin^2 \theta_{\text{slow}}) \sin(2\theta_{\text{slow}}) \\ & - \Psi_{\text{CP}} B_{\text{env}}^{\text{NF}^2}(t) \sin 2\theta_{\text{slow}} + O(\theta_{\text{fast}}^3). \end{aligned} \quad (5-18)$$

Here, $\langle \cdots \rangle_{\tau} = 1/\tau \int_t^{t+\tau} d\tau \cdots$ is the temporal average over a single oscillation period of $B_{\text{THz}}^{\text{NF}}$, $\tau = 2\pi/\omega$, and we used the following assumptions: (a) $\langle \theta_{\text{fast}} \rangle_{\tau} = \langle \dot{\theta}_{\text{fast}} \rangle_{\tau} = \langle \ddot{\theta}_{\text{fast}} \rangle_{\tau} = 0$ and (b) the change in $B_{\text{env}}^{\text{NF}}(t)$ proceeds much slower than that of the ac field oscillation. Therefore, we treat $B_{\text{env}}^{\text{NF}}(t)$ as a constant within each temporal period for averaging, that is, $\langle B_{\text{env}}^{\text{NF}}(t) \rangle_{\tau} \approx B_{\text{env}}^{\text{NF}}(t)$.

Eq. (5-19) shown below describes the analytical solution for θ_{fast} which oscillates with the same frequency as the THz magnetic field. By substituting Eq. (5-19) for θ_{fast} into Eq. (5-18), the equation of motion for θ_{slow} can be rewritten as shown in Eq. (5-20).

$$\theta_{\text{fast}} \approx \frac{\chi \sin \theta_{\text{slow}} B_{\text{env}}^{\text{NF}}(t)}{\omega^2} \cos(\omega t), \quad (5-19)$$

$$\begin{aligned} \ddot{\theta}_{\text{slow}} + c \dot{\theta}_{\text{slow}} &= -\chi \sin \theta_{\text{slow}} B_{\text{DC}} - \frac{a}{2} (b + \sin^2 \theta_{\text{slow}}) \sin(2\theta_{\text{slow}}) \\ &\quad - \Psi_{\text{ZT}} B_{\text{env}}^{\text{NF}^2}(t) \sin(2\theta_{\text{slow}}) - \Psi_{\text{CP}} B_{\text{env}}^{\text{NF}^2}(t) \sin(2\theta_{\text{slow}}) \\ &= -\frac{\partial W_{\text{eff}}}{\partial \theta_{\text{slow}}}, \end{aligned} \quad (5-20)$$

$$\Psi_{\text{ZT}} = \frac{\gamma^4 H_D^2}{4\omega^2}. \quad (5-21)$$

$$\Psi_{\text{CP}} = \frac{\gamma^2 \omega^2 (\omega_{\text{AFM}}^2 - \omega^2)}{4((\omega_{\text{AFM}}^2 - \omega^2)^2 + (\omega c)^2)}. \quad (5-22)$$

Eq. (5-20) describes the motion of θ_{slow} including the effect of the THz magnetic pulse, and the right-hand side can be seen as the driving force. The second-order terms of $B_{\text{env}}^{\text{NF}}$ come from the first and the fifth terms on the right-hand side of Eq. (5-18). The effective potential for θ_{slow} is given by the integration of the force, as shown in Eq. (5-23):

$$W_{\text{eff}}(\theta_{\text{slow}}) = W_0(\theta_{\text{slow}}) + W_{\text{ZT}}(\theta_{\text{slow}}) + W_{\text{CP}}(\theta_{\text{slow}}), \quad (5-23)$$

$$W_0(\theta_{\text{slow}}) = \frac{ab}{2} \sin^2 \theta_{\text{slow}} + \frac{a}{4} \sin^4 \theta_{\text{slow}} - \chi B_{\text{DC}} \cos \theta_{\text{slow}}, \quad (5-24)$$

$$W_{\text{ZT}}(\theta_{\text{slow}}) = \frac{\chi^2 B_{\text{env}}^{\text{NF}^2}(t) \sin^2 \theta_{\text{slow}}}{4\omega^2}, \quad (5-25)$$

$$W_{\text{CP}}(\theta_{\text{slow}}) = \frac{\gamma^2 \omega^2 (\omega_{\text{AFM}}^2 - \omega^2) B_{\text{env}}^{\text{NF}^2}(t) \sin^2 \theta_{\text{slow}}}{4((\omega_{\text{AFM}}^2 - \omega^2)^2 + (\omega c)^2)}. \quad (5-26)$$

W_{eff} is the effective potential written as the sum of the potential at equilibrium W_0 and the additional term W_{ZT} as well as W_{CP} which represents the change in the potential that occurs when the spin system is exposed to the time-periodic

THz magnetic field $B_{\text{THz}}^{\text{NF}}$. W_{ZT} and W_{CP} are due to the Zeeman torque directly exerted by the THz magnetic near field and the coupling between the THz magnetic near field, the q-AFM and q-FM modes, respectively. ω_{AFM} is the frequency of the q-AFM mode. When the frequency of the time-periodic magnetic field was approaching the q-AFM resonance, the potential modification would be greatly enhanced.

We can unify the contributions from the pure THz magnetic field (Ψ_{ZT}), and from the mixture of THz magnetic field, the q-AFM mode and q-FM mode (Ψ_{CP}). Due to the torque $\mathbf{M} \times \mathbf{B}_{\text{THz}}^{\text{NF}}$ (the first term on the right-hand side of Eq. (5-5), $\mathbf{M} \times \mathbf{B}_{\text{THz}}^{\text{NF}} \propto \sin\theta B_{\text{THz}}^{\text{NF}}$), $B_{\text{THz}}^{\text{NF}}$ excites the fast-swing motion of $\mathbf{L}$ in a - c plane (θ_{fast}) via forced oscillation synchronized with $B_{\text{THz}}^{\text{NF}}$. In turn, the fast oscillation of θ_{fast} modifies the torque dynamically, because of $\mathbf{M} \times \mathbf{B}_{\text{THz}}^{\text{NF}} \propto B_{\text{THz}}^{\text{NF}} \sin(\theta_{\text{fast}} + \theta_{\text{slow}})$. Finally, the time average of $\theta_{\text{fast}} B_{\text{THz}}^{\text{NF}}$ induces a DC (or accurately, slowly-varying) component and thus excite the slow pendulum motion of $\mathbf{L}$. Similarly, because of the torque $\mathbf{M} \cdot \dot{\mathbf{B}}_{\text{THz}}^{\text{NF}}$ (the second term on the right-hand side of Eq. (5-8), $\mathbf{M} \cdot \dot{\mathbf{B}}_{\text{THz}}^{\text{NF}} \propto \cos\theta \dot{B}_{\text{THz}}^{\text{NF}}$), the fast oscillation of the amplitude of $\mathbf{M}$ (q-AFM mode) is excited via forced oscillation with the same frequency as $B_{\text{THz}}^{\text{NF}}$. In turn, the fast oscillation of the amplitude of $\mathbf{M}$ (the third term on the right-hand side of Eq. (5-5), $\Delta M \propto |\dot{\mathbf{L}} \times \mathbf{L}| \propto \dot{\phi} \cos\theta$) modifies the torque $\mathbf{M} \times \mathbf{B}_{\text{THz}}^{\text{NF}}$ dynamically (the third term on the right-hand side of Eq. (5-5), $\mathbf{M} \times \mathbf{B}_{\text{THz}}^{\text{NF}} \propto \sin\theta B_{\text{THz}}^{\text{NF}}$). Therefore, the time average of $M B_{\text{THz}}^{\text{NF}}$ induces a DC component and thus excite the slow pendulum motion of $\mathbf{L}$.

5.4.4 Physical mechanism of spin-switching excitation

The excitation of spin switching can be understood as follows. As shown in the schematics of Fig. 5-12c, before the THz magnetic field is applied, W_{eff} is equal to W_0 , and thus W_{eff} exhibits a double-well shape with a small barrier centered at $\theta = 90^\circ$ (the barrier height is denoted by h and the left potential minimum is at $\theta_L = 75^\circ$). In process 1, the strong periodic THz magnetic near field modifies the potential significantly ($W_{\text{eff}} = W_0 + W_{\text{ZT}} + W_{\text{CP}}$): the new

minimum, $\theta_{L,\text{Floq}}$, reaches values well below the initial local minimum θ_L and the barrier height at the center, h_{Floq} , becomes much larger than h . Thus, as indicated by the orange arrow in process 1, the change in the slope of W_{eff} causes a rotation of $\mathbf{L}$ away from the barrier, and this explains the observed peculiar “downward” movement of $\Delta\eta$. When the strong magnetic field disappears, the potential energy returns to W_0 and $\mathbf{L}$ is not located at its equilibrium position, and then a free oscillation of $\mathbf{L}$ starts (process 2) due to inertia effect. When $\mathbf{L}$ has been driven sufficiently far away from the barrier during process 1, $\mathbf{L}$ can accumulate enough “kinetic energy” and thus spin switching can be achieved in the following inertia motion of $\mathbf{L}$ (process 3). The term “kinetic energy” refers to $\dot{\theta}^2/2$, since the equation of motion contains the term $\ddot{\theta}$, which corresponds to the acceleration term in Newton’s equation of motion with unit mass²³.

Finally, on the basis of the driving force of the slow oscillation (this force is determined by the effective potential as shown in Eq. (5-20)), a quadratic dependence of the slow component of $\Delta\eta$ on $B_{\text{amp}}^{\text{NF}}$ can be obtained (The process of derivation, carried out by Mr. Kanega and Dr. Sato from Chiba University, is presented in the Section XI of Supplementary Information of the reference⁹¹.), which is consistent with the observed quadratic dependence of $\Delta\eta$ in Figs. 5-5b and 5-7c.

5.4.5 Comparison between sine-Gordon equations without/with effective-potential approximation

Finally, we verified that the obtained sine-Gordon equation using effective-potential approximation Eq. (5-20) (SG (W_{eff})) is valid by comparing its numerical solutions to the sine-Gordon equation Eq. (5-5) without the approximation (SG).

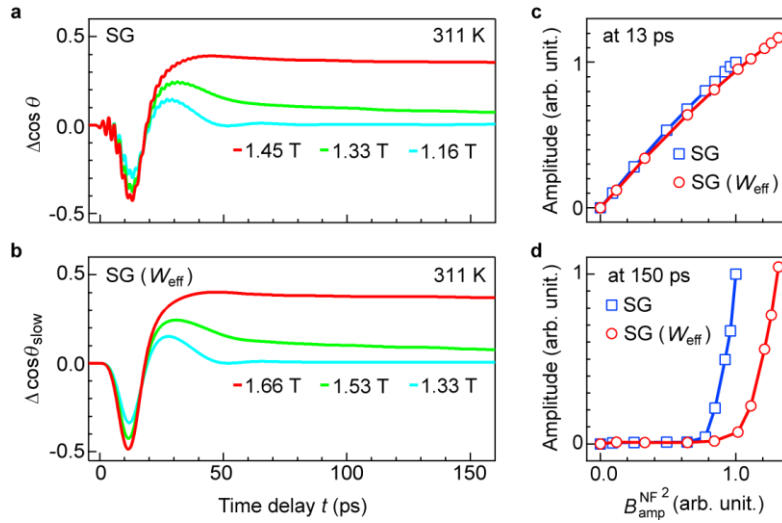


Figure 5-13. The calculational results of the sine-Gordon equations including the thermal fluctuation. The curves in **a** and **b** are the results of the sine-Gordon equation Eq. (5-5) and the sine-Gordon equation with effective-potential approximation Eq. (5-20), respectively. The amplitudes of the slow motion at 13 ps and at 150 ps are given in **c** and **d**, respectively. Figure reprinted with permission from the reference⁹¹.

The numerical solutions of SG (W_{eff}) is shown in Fig. 5-13b. Because the fast oscillations are averaged in the derivation process, we cannot observe the fast oscillations. They exhibit the same slow motions as the results of SG in Fig. 5-13a. The amplitudes of slow motion at 13 ps based on the two questions are shown in Fig. 5-13c. We found that the two equations almost lead to the same results which verifies the effective-potential approximation is reasonable. It indicates that effective potential W_{eff} can be used to explain the excitation of the slow motion.

However, as shown in Fig. 5-13d, SG (W_{eff}) requires a higher field amplitude to achieve spin switching than SG. The main reason can be explained by using Fig. 5-14. In Fig. 5-14a, we compared the results of SG with pump amplitude 1.45 T and SG (W_{eff}) with pump amplitude 1.53 T. To better observe the slow motion, the result of SG is filtered to exclude the fast oscillation. We found although at 13 ps, the slow motions have the same amplitudes, the curve of SG finally overcomes the barrier, but another one cannot overcome the barrier. It is because, as shown by the first-order derivative with respect to time, from 13

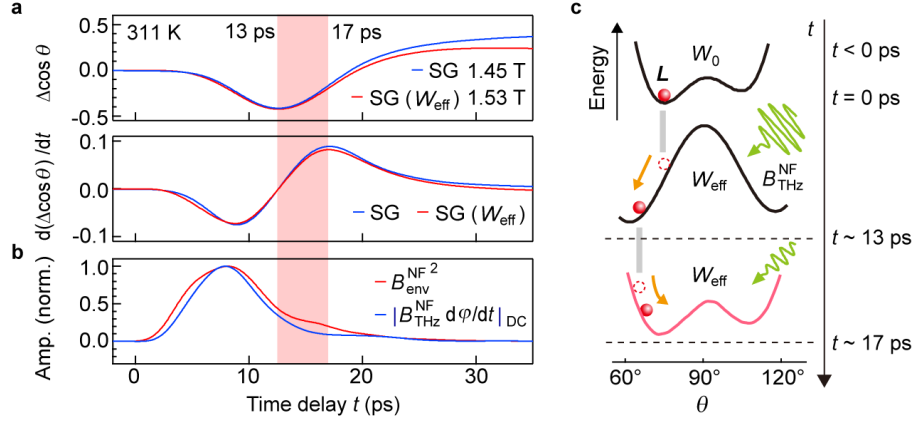


Figure 5-14. The curves in **a** are the calculational results and corresponding time derivatives obtained by solving the sine-Gordon equation Eq. (5-5) and the sine-Gordon equation with effective-potential approximation Eq. (5-20) including the thermal fluctuation. The curves in **b** are square of envelope used in Eq. (5-20) and the DC component of $B_{\text{THz}}^{\text{NF}} \dot{\phi}$ used in Eq. (5-5). The shaded area refers to the time range from 13 ps to 17 ps. The motion of L in potential between 0 ps and 17 ps is shown in (c). Figure reprinted with permission from the reference⁹¹.

ps to 17 ps, the speed of L moving right in the potential predicted by SG (W_{eff}) gradually becomes smaller than that of SG.

In the derivation of SG (W_{eff}), the amplitude of $\dot{\phi}$ is assumed to completely vary with $B_{\text{env}}^{\text{NF}}$, thus the DC component of the term $\dot{\phi} B_{\text{THz}}^{\text{NF}}$ finally is proportional to the square of $B_{\text{env}}^{\text{NF}}$. But in fact, a little deviation exists as shown in Fig. 5-14b and is included by SG. In the time range from 13 ps to 17 ps, $|\dot{\phi} B_{\text{THz}}^{\text{NF}}|_{\text{slow}}$ decreases faster than $(B_{\text{env}}^{\text{NF}})^2$, and leads to the smaller potential modification. Therefore, $|\dot{\phi} B_{\text{THz}}^{\text{NF}}|_{\text{slow}}$ in SG causes the smaller resistance for L moving right as shown in Fig. 5-14c (the force due to the additional potential energy is proportional to $-\sin 2\theta_{\text{slow}}$, which is a negative value and pushes L towards left side.), and makes the spin switching easier.

In summary, although SG (W_{eff}) and SG lead to a little difference in switching threshold, using the effective potential to predict why and how large the slow motion is excited is still reasonable.

5.5 Relation to Floquet engineering

The consistent results of direct solution and the solution with the effective-potential approximation indicate that the potential energy of the system is dynamically modified by the multicycle THz magnetic near field. This mechanism is similar as Floquet engineering which is often studied in the electron systems¹²⁶.

In our work, a DC component is introduced to the potential energy during the process where the magnon (a quasiparticle that represents the quanta of spin dynamics in a magnetic system.) is excited from the ground state to the virtual state and then drops back to the ground state. If the virtual state is near a real energy level (q-AFM mode), the excitation into the virtual state will be enhanced and thus the DC component will become larger. This is the similar process depicted in the Floquet engineering where a system interacts with the time-periodic external field by absorbing one $\hbar\omega$ photon and simultaneously emitting one $\hbar\omega$ photon¹²⁷. According to the Floquet theory, this interaction process generates a DC component to the effective Hamiltonian of the system.

Importantly, at the actual high-frequency limit where the frequency of the THz magnetic field is far higher than those of the q-FM and q-AFM modes, the effective potential energy in Eq. (5-23) is same as that obtained by the method of Floquet-Magnus expansion¹²⁰ (The process of derivation, carried out by Mr. Kanega and Dr. Sato from Chiba University, is presented in the Section X of Supplementary Information of the reference⁹¹). Therefore, we can conclude that the effective potential is the result of the Floquet engineering driven by the multicycle THz magnetic field.

5.6 Discussion

5.6.1 Response as the function of the pump-pump delay

To further verify the excitation mechanism of q-FM mode, we performed the

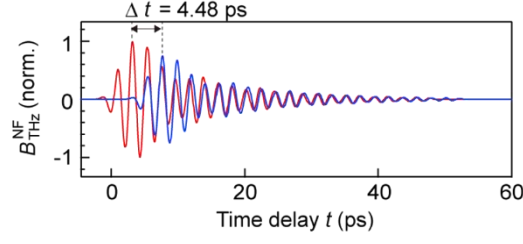


Figure 5-15. Definition of Δt . Figure reprinted with permission from the reference⁹¹.

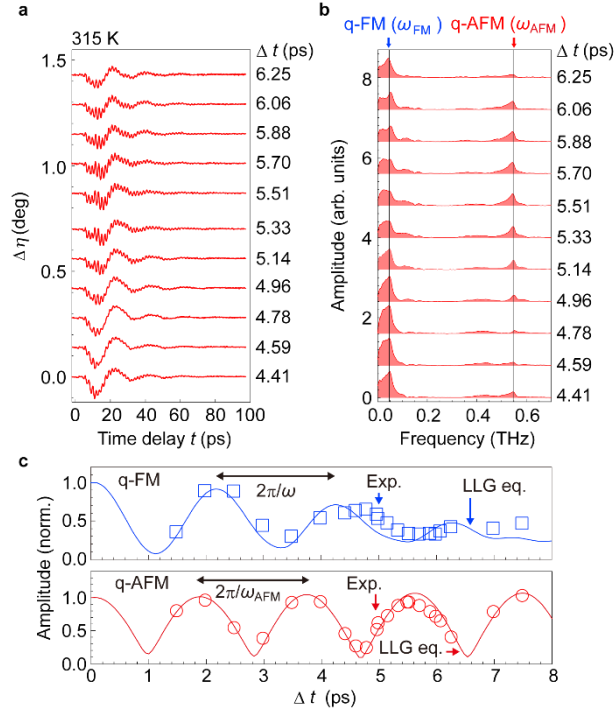


Figure 5-16. Experimental results for different delay times Δt between the two pulses of the THz double-pump pulse. **a**, The temporal evolution of the ellipticity-angle change at 315 K. **b**, The corresponding spectra, where the frequencies of the q-FM mode ω_{FM} and the q-AFM mode ω_{AFM} are indicated. **c**, The observed peak amplitudes of the q-FM mode (blue squares) and the q-AFM mode (red circles) extracted from the data in **b**. The blue and red curves are the calculation results by numerically solving the LLG equations. Figure reprinted with permission from the reference⁹¹.

experiment by varying the pump-pump delay Δt of THz double-pump pulses as shown in Fig. 5-15. For better observation of both the q-FM and q-AFM modes, the temperature is set 315 K. The temporal evolutions of $\Delta\eta(t)$ for excitation using different values of Δt are shown in Fig. 5-16a, the corresponding spectra are shown in Fig. 5-16b and the amplitudes of the q-FM and the q-AFM modes are shown in Fig. 5-16c. We find that the amplitudes of the q-FM and q-AFM

modes as the functions of Δt can be well reproduced by the numerical calculation using the LLG equations.

In the double-pump experiment, the amplitude of a response varies with pump-pump delay Δt due to the interferences. The interferences have two origins. One is the interference between the responses which reflects the frequency of the response. And another one is the interference between the double-pump pulses at a specific frequency which is responsible for the excitation of the response. The interference period of the latter one reveals the excitation frequency of the response.

The frequency of the q-FM mode is about 0.05 THz, thus the interference period between two q-FM modes is 20 ps. Due to the large damping effect, the first type of interference cannot be observed in this experiment. Therefore, the interference period reveals the excitation frequency of the q-FM mode. As shown in Fig. 5-16c, the period $2\pi/\omega$ in the Δt axis of the q-FM mode indicates that both the Zeeman-torque term W_{ZT} and the coupling term W_{CP} are contributed by the forced oscillations which are expressed by Eqs. (5-10) and (5-19). In the calculation, we used $\omega_{\text{AFM}}/2\pi = 0.54$ THz, $\omega_{\text{FM}}/2\pi = 0.05$ THz at 315 K and $\omega/2\pi = 0.46$ THz.

5.6.2 Reversal of bias magnetic field

To verify that the initial state does not influence the behavior of the slow motion and spin switching, we reverse the bias magnetic field to change the initial state of the magnetization. As shown in Fig. 5-17, $\mathbf{L}$ can be either initialized at θ_{L} or θ_{R} , depending on the direction of B_{DC} . The signs of $\Delta\eta$ of both the slow oscillation and spin switching are reversed in these two cases, but in either case $\mathbf{L}$ is initially driven away from the barrier, which supports our analysis based on the effective-potential approximation.

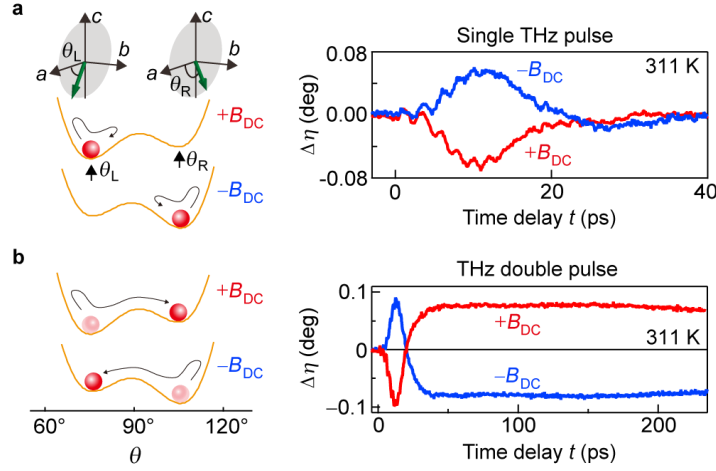


Figure 5-17. Opposite initial states of magnetization. The initial direction of $\mathbf{L}$ with respect to a axis is determined by the direction of bias magnetic field $\mathbf{B}_{DC}$ as shown in the left panel. For both single THz-pulse pumping and THz double-pulse pumping, the signals are reversed if the initial direction is changed from θ_L to θ_R . Figure reprinted with permission from the reference⁹¹.

5.6.3 Influence of THz electric field

To investigate the influence of the THz electric field on $\Delta\eta$, we fabricated a gold bow-tie antenna³³ with a gap of 4 μm (Fig. 5-18), which can only generate a THz electric near field. The predicted peak amplitude of THz electric near field at the center of the gap exceeds 1.3 MV/cm, which is much stronger than the THz electric near field in the spiral microstructure. The angle between the short edge of the antenna (along x axis in Fig. 5-18b) and b axis of the material is 30° to ensure that both the electronic orbital transitions^{32,33} and the THz inverse Cotton–Mouton effect¹²⁸ can be induced by the THz electric near field. The experimental conditions were same as those mentioned in the above sections (the sample temperature was 315 K, where the excitation of both the q-AFM mode and the q-FM mode is possible). The ellipticity-angle change probed at the center of the gap is shown in Fig. 5-18c, which evidences that the THz electric near field cannot excite the q-AFM mode and also not the q-FM mode near room temperature. The observed rapid oscillation in the time range

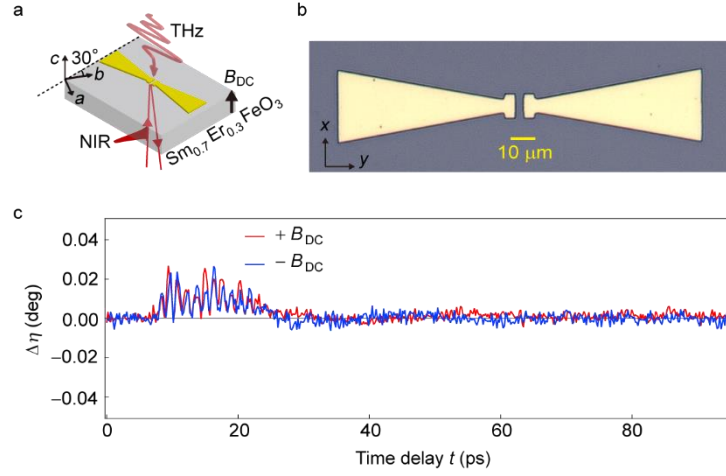


Figure 5-18. Experimental results obtained using a THz electric near field. (a) Schematic of the gold bow-tie antenna on $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$. The polarization direction of the incident THz electric field is parallel to the antenna extension and the probe pulse is polarized along b axis of $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$. (b) Photograph of the fabricated gold bow-tie antenna. (c) The temporal evolution of the ellipticity-angle change induced by a THz electric near field for different directions of B_{DC} at 315 K. The initial direction of L with respect to a axis is determined by the direction of B_{DC} . Figure reprinted with permission from the reference⁹¹.

$t < 25$ ps is due to the THz Kerr effect^{30,99}, which does not depend on the direction of the bias magnetic field B_{DC} .

5.6.4 Dynamics of M and L along three axes

After calculation of Eqs. (5-5) and (5-8), we obtain temporal development of θ (q-FM mode) and φ (q-AFM mode). $\Delta\cos\theta$ is used to explain the motion of q-FM mode exhibited by experimental results $\Delta\eta$. The rationality is explained in this section. As discussed in section 4.6, the magneto-optic signal $\Delta\eta$ reflects the dynamics of ΔM_c and ΔL_a . ΔM_c and ΔL_a change due to the q-AFM and q-FM modes. We will show that the q-FM-mode components of ΔM_c and ΔL_a can be expressed as the function of $\Delta\cos\theta$.

The dynamics of all components of M and L are calculated using LLG equations (Eqs. (2-3) – (2-5)) and are shown in Figs. 5-19a and b, where the

fast and slow motions refer to the q-AFM and q-FM modes, respectively.

We found that during motion, for both the vector $\mathbf{M}$ and $\mathbf{L}$, the b -axis components are very small: $|M_b/M_0|, |L_b/L_0| \leq 0.15$ (M_0 and L_0 are the lengths of $\mathbf{M}$ and $\mathbf{L}$ at equilibrium, respectively). Therefore, the projected lengths of $\mathbf{M}$ and $\mathbf{L}$ in a - c plane are almost same as the vector lengths of $\mathbf{M}$ and $\mathbf{L}$, respectively. In addition, we know that the q-FM mode is described by the swing motions of $\mathbf{M}$ and $\mathbf{L}$ in a - c plane. We will verify that the swing motions of $\mathbf{M}$ and $\mathbf{L}$ in a - c plane can be described by using only one angle. We compare the dynamics of the angle θ_{MV} (between the component of $\mathbf{M}$ in a - c plane and c axis) and the angle θ_{LV} (between the component of $\mathbf{L}$ in a - c plane and a axis) as defined in Fig. 5-19c. The results in Fig. 5-19d show that the dynamics of θ_{LV} are equivalent to those of θ_{MV} . Therefore, we can conclude that the use of θ is sufficient to describe the swing motions of $\mathbf{M}$ and $\mathbf{L}$ in a - c plane.

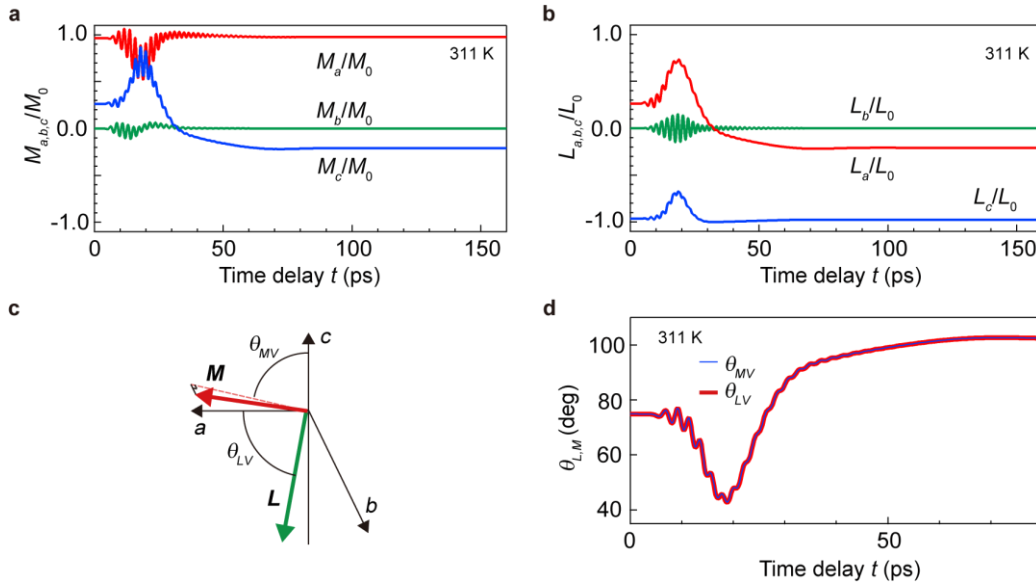


Figure 5-19. Comparison between all components of $\mathbf{M}$ and $\mathbf{L}$ calculated by the LLG equations, Eqs. (2-3) – (2-5). **a**, The time traces of M_a/M_0 (red curve), M_b/M_0 (green curve) and M_c/M_0 (blue curve). M_0 is the amplitude of $\mathbf{M}$ at equilibrium. **b**, The time traces of L_a/L_0 , L_b/L_0 and L_c/L_0 . L_0 is the amplitude of $\mathbf{L}$ at equilibrium. **c**, The definitions of θ_{MV} and θ_{LV} . The former angle is the angle between the component of $\mathbf{M}$ in a - c plane and c axis. θ_{LV} is the angle between the component of $\mathbf{L}$ in a - c plane and a axis. **d**, The time traces of θ_{MV} and θ_{LV} . Figure reprinted with permission from the reference⁹¹.

Based on the discussions above, we obtain the relation, $M_c \approx M \cos \theta$ and $L_a \approx L_0 \cos \theta$, where M is the vector length of $\mathbf{M}$. Due to the existence of the q-AFM mode, M oscillates rapidly which can be confirmed by observing M_c/M_0 in Fig. 5-19a. Because the q-AFM mode is much faster than the q-FM mode and the oscillation center of M is M_0 , to describe the q-FM mode, we can ignore the component of q-AFM mode in M_c and obtain $\Delta M_c \approx M_0 \Delta \cos \theta$ as well as $\Delta L_a \approx L_0 \Delta \cos \theta$.

5.6.5 Back switching driven by stronger THz magnetic field

We can speculate what will happen as the field strength of the magnetic field becomes stronger. Additional calculations are performed for field strengths up to 140% of the value (1.45 T) that reproduces the experiment at maximum power. As shown in Fig. 5-20, a non-monotonic field-strength dependence can be observed, indicating that switching occurs only within a certain intermediate regime. If the field amplitude of the THz magnetic field is just a little larger than 1.45 T, apart from the switching, a few oscillation cycles around the second potential minimum can be observed which is attributed to the excess kinetic energy after switching. If the THz magnetic field is too strong (2.03 T), back-switching occurs, because the kinetic energy becomes too large to relax into the second potential minimum.

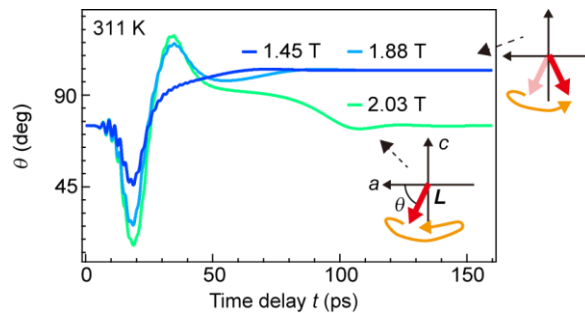


Figure 5-20. The predicted behaviour of θ for THz magnetic fields stronger than the value (1.45 T) that reproduces the experiment at maximum power. Figure reprinted with permission from the reference⁹¹.

5.6.6 Influence of the frequency of THz magnetic field

To investigate the influences of the frequency of THz magnetic field on the nonlinearly excited spin dynamics, the original sine-Gordon equation and the equation rewritten using the effective potential (Eqs. (5-5) and (5-20), respectively) are numerically solved, as shown in Fig. 5-21. In these calculations, the temperature was set to 315 K, where the frequency of the q-FM (q-AFM) mode is 0.05 THz (0.54 THz). Here, we used the idealized magnetic pulse $B_{\text{env}}^{\text{NF}}(t)\cos(\omega t)$ (Fig. 5-21a), where the temporal variation of $B_{\text{env}}^{\text{NF}}(t)$ is much slower than that in the actual experiment. For comparison of the slow motion of the magnetic order, a low-pass filter was applied to the results of Eq. (5-5). The results for different carrier frequencies are shown in Figs. 5-21b, c, d, e and f.

Because the envelope of the magnetic pulse varies slower than the decay rate of q-FM mode, we find that the magnetic order here almost keeps staying at the potential minimum during the modification of the potential W_{eff} (adiabatic process). Because there is no “inertia”-driven motion after the magnetic pulse, q-FM-mode oscillation and spin switching cannot occur.

Regarding the influence of the carrier frequency, we find that, when the frequency of the magnetic pulse is very low (e.g. 0.12 THz) and is close to the resonance frequency of the q-FM mode (0.05 THz), the results of Eqs. (5-5) and (5-20) are clearly different, which indicates that the motion equation using the effective potential W_{eff} to describe the spin dynamics is not valid. On the other hand, when the magnetic pulse has a sufficiently high frequency ≥ 0.3 THz, the results of Eqs. (5-5) and (5-20) are almost identical, which indicates that the system is in the dynamically modified state defined by W_{eff} . As predicted by the coupling term defined in Eqs. (5-23) and (5-26), when the carrier frequency is equal to the frequency of the q-AFM mode, the potential modification becomes very small. When the carrier frequency exceeds the frequency of the q-AFM mode, the sign of the potential modification changes.

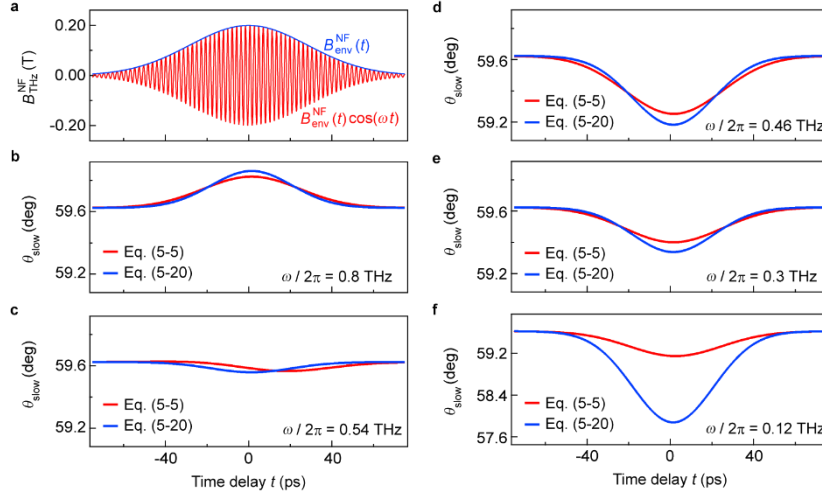


Figure 5-21. The solutions of Eqs. (5-5) and (5-20). **a**, An idealized THz magnetic pulse at 0.46 THz (red curve) with a slowly varying envelope function (blue curve). **b**, By using the functions $B_{\text{env}}^{\text{NF}}(t)\cos(\omega t)$ and $B_{\text{env}}^{\text{NF}}(t)$ [shown in a] in Eqs. (5-5) and (5-20), respectively, we can obtain approximately the same solutions when $\omega/2\pi = 0.8$ THz: The red curve represents the dynamics of θ derived using Eq. (5-5), and the blue curve represents the dynamics of θ_{slow} derived using Eq. (5-20). The panels **c**, **d**, **e** and **f** show the solutions obtained for $\omega/2\pi = 0.54$ THz, 0.46 THz, 0.3 THz and 0.12 THz, respectively. Figure reprinted with permission from the reference⁹¹.

5.7 Summary

Our work provided a novel method for ultrafast spin switching which is significant for advancing research about spintronics. We realized the spin switching using THz magnetic field for the first time. The spin switching is driven by the THz-field-modified potential energy. There is a detail: (i) During the excitation, the Tesla-class multicycle magnetic fields interact with the spin orders, and thus reshape the potential energy, which is similar as the process of Floquet engineering; (ii) As a result, the spin order $\mathbf{L}$ is driven away from the barrier in the potential energy leading to the excitation of the q-FM mode; (iii) In the subsequent inertial motion, $\mathbf{L}$ finally goes across the barrier and relaxes to the second potential minimum.

In addition, as predicted by Eqs. (5-23) and (5-26), we can expect to control the position of the potential minima and the height of the potential barrier by applying the THz magnetic field and tuning its amplitude and frequency. It is equivalent with spin reorientation transition induced by varying temperature as shown by Eqs. (5-1) and (5-2). In contrast to temperature, using THz magnetic pulse provides the possibility to realize ultrafast spin reorientation transition which is important for the information storage and processing in spintronics. Furthermore, our results indicate that driving magnetic order parameters via dynamically stabilized states may be a way to design functional properties of various materials¹³, including atomic layers of magnetic materials¹²⁹ and quantum spin systems¹¹⁰, and this may lead to new optoelectronic and coherent spintronic devices^{11,130}.

Chapter 6 Conclusion

In this thesis, we investigated the ultrafast manipulation of spin orders by exciting the coherent spin dynamics into the nonlinear regime using the THz magnetic fields in the canted antiferromagnets HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$.

Due to the robust antiferromagnetic exchange interaction, the spin dynamics lie in the THz frequency range, enabling manipulation on the picosecond timescale. In contrast to the ultrafast manipulation using the electric fields of NIR, MIR, and THz pulses, THz magnetic fields do not excite the electron and lattice states but directly excite the spin dynamics. This makes THz magnetic fields the most versatile across various materials and temperatures. The studies on nonlinear spin dynamics using THz magnetic fields become feasible owing to the technology for generating intense THz pulses and the novel microscopic structure SAR, which can convert the intense THz pulses into the Tesla-class THz magnetic near fields. By analyzing the time-resolved spin dynamics, we revealed how the anharmonicities of the potential energies of spin orders affect the spin dynamics.

The spin dynamics in canted antiferromagnets have two eigenmodes. In chapter 4, we studied the nonlinearities of the q-AFM mode in HoFeO_3 . We chose an experiment configuration to ensure that only the q-AFM mode is excited. Under weak excitation, the time-resolved magneto-optic signal exhibits an oscillation at the frequency of the q-AFM mode. As the excitation become strong, the oscillation exhibits an asymmetric envelope, and the spectrum shows the second- and third-order-harmonic peaks, as well as the frequency redshift of the q-AFM mode. We investigated the origins of these phenomena based on the LLG equations. From the LLG equations, we derived the motion equation of the q-AFM mode which features an anharmonic potential energy proportional to the square of the sine function. Under the weak perturbation, spins oscillate near the minimum and the potential energy can be

approximately considered a harmonic parabolic function. But, under the strong excitations, the anharmonicities cannot be ignored, thus leading to the third-order harmonic generation and the frequency redshift. In addition, the asymmetric envelope and the second-order harmonic generation are attributed to the nonlinearities of the magneto-optic effect related to the q-AFM mode which can be reproduced well by the numerical solution of the motion equation of q-AFM mode and the wave equation of probe pulses transmitting through the sample. These results reveal that the anharmonic potential energy and the magneto-optic effect both play a significant role in observing the nonlinearities of the q-AFM mode.

In chapter 5, we studied the nonlinear spin dynamics in the potential energy of the q-FM mode in $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$. As the field strength of the THz magnetic field is increased beyond a critical value, spin switching occurs. From the experimental results, we found that before the excitation, spins are in the first minimum of the potential energy; during the THz multicycle magnetic field, spins are driven away from the potential barrier; after the field, spins move backwards and finally overcome the barrier relaxing to the second potential minimum. To explain this behavior, we derived the motion equation of the q-FM mode (sine-Gordon equation) from the LLG equations. We found that the potential energy of the q-FM mode includes the Zeeman torque of the THz magnetic field, as well as the coupling between the THz magnetic field and the q-FM and q-AFM modes. Due to the experiment configuration, both terms are nonzero, thus responsible for the excitation of q-FM mode and spin switching. We analytically solved the sine-Gordon equation by replacing the potential energy interacting with the fast-oscillating magnetic field with a “time-averaged” effective potential that varies with the envelope of the field. At the high-frequency limit of the THz magnetic field, the effective potential energy is consistent with the result of Floquet-Magnus expansion, indicating that the effective potential energy is constructed similarly as the Floquet engineering. Under our experiment condition, as the THz magnetic field increases, the barrier between double minima of the effective potential energy grows (becomes higher and broader), thus pushing spins away from the barrier. After

the THz magnetic field vanishes, the effective potential energy recovers to the static shape, thus spins move backwards. In the subsequent inertial motion, spins finally go across the barrier and relax to the second potential minimum. These results suggest that the THz magnetic field is a new method for ultrafast spin switching, while also exhibiting a potential to dynamically modify the potential energy of spin orders.

In this thesis, we summarize the nonlinear coherent dynamics of the q-AFM and q-FM modes in HoFeO_3 and $\text{Sm}_{0.7}\text{Er}_{0.3}\text{FeO}_3$, respectively. The observed frequency redshift and the third-order harmonic of the q-AFM mode reflect the anharmonic potential energy for the q-AFM mode. Regarding the q-FM mode, we observed an extremely nonlinear phenomenon, spin switching. The excitation process responsible for spin switching is an intriguing nonlinear process where a multicycle THz magnetic field modifies the potential for the q-FM mode. Our investigations show that THz magnetic fields are potentially useful for the investigation of coherent spin nonlinearities and are novel methods for ultrafast manipulation of spin states.

Finally, we will discuss future prospects and challenges. The results of our works are considered highly important for future applications in ultrafast spintronics. Driving the antiferromagnetic vector out of equilibrium with a large amplitude offers a potential method for spin pumping (a process of spin-charge conversion); ultrafast non-thermal switching of the antiferromagnetic vector is significant for the information storage and processing. For the application, the THz-pulse generation and the magnetic-near-field generation should be integrated onto the surface of the antiferromagnets. The on-chip experiments to generate and detect the THz electric near field using the photoconductive switches have been broadly studied^{131–134}, and we expect that these technologies can be applied to the THz magnetic near field. For the fundamental research, our results can extend beyond enhancing our understanding of spin nonlinearity and the potential applications of antiferromagnets. They indicate that driving magnetic order parameters via dynamically stabilized states may provide a method to design the functional

properties of various materials, including atomic layers of magnetic materials and quantum spin systems. This approach could potentially lead to the development of new optoelectronic and coherent spintronic devices.

Appendix

A1. Details of the simulation model including fluctuations

In order to reproduce the behaviour of the experimentally observed relaxation process after spin switching (e.g. the slow decay of the data for $0.98 \times B_{\max}^{\text{NF}}$ shown in Fig. 5-7 in the main text), the sine-Gordon equation given in Eq. (5-5) was extended to take the effects of thermal fluctuations (due to a non-zero temperature) and the impact of the presence of domains with different magnetization directions into account. Because the physics described by Eq. (5-8) do not govern characteristic features of the observed spin-switching process, this equation does not require an extension. Below we explain the derivation of this extended equation.

Firstly, when $\mathbf{L}(\mathbf{M})$ is located at the minimum at $\theta > 90^\circ$ (which has a higher energy than the other minimum at $\theta < 90^\circ$ as shown in Fig. 5-3b), the thermal fluctuations that are present in a real sample let $\mathbf{L}(\mathbf{M})$ switch back to the minimum at $\theta < 90^\circ$ after some time, which leads to an exponential decay of $\Delta\eta$ with a certain relaxation time constant. In the presence of thermal fluctuations, the time evolution of $\mathbf{L}(\mathbf{M})$ depends on the temporal sequence of a force due to thermal fluctuations (i.e., a random force), as shown in the following discussion. Therefore, we have to calculate the ensemble average of many time evolutions of $\mathbf{L}(\mathbf{M})$ for different sequences of the random force, and the dynamics of the averaged $\mathbf{L}(\mathbf{M})$ should correspond to the experimentally measured dynamics. In this sense, we may regard the $\mathbf{L}(\mathbf{M})$ of each ensemble as a local magnetic order parameter in a mesoscopic system. This means that we separate the macroscopic magnetization in the considered volume into many mesoscopic spin ensembles, where each mesoscopic spin ensemble perceives a random force (uncorrelated to all other spin ensembles). Below, Eq. (5-5) with

an additional term for thermal fluctuations is used as the equation of motion for such a local magnetization $\mathbf{M}$. The considered equation reads

$$\begin{aligned} \ddot{\theta} + c\dot{\theta} = & -\chi(B_{\text{DC}} + B_{\text{THz}}^{\text{NF}}(t))\sin\theta - a\sin\theta\cos\theta(\sin^2\theta + b) \\ & + 2\gamma B_{\text{THz}}^{\text{NF}}(t)\dot{\phi}\cos\theta\sin\theta + \gamma\dot{B}_{\text{THz}}^{\text{NF}}(t)\phi\cos\theta\sin\theta + R(t), \end{aligned} \quad (\text{A1-1})$$

where θ is the angle between the mesoscopic net magnetization $\mathbf{L}(\mathbf{M})$ and $a(c)$ axis. The new term $R(t)$ corresponds to the random force due to thermal fluctuations. Following the Langevin equation approach¹³⁵, we can define the force-term $R(t)$. It satisfies the following two conditions:

$$\langle R(t) \rangle = 0, \quad (\text{A1-2})$$

$$\langle R(t)R(t') \rangle = 2D\delta(t - t'). \quad (\text{A1-3})$$

The symbol $\langle \dots \rangle$ denotes the average over all ensembles, namely the average over all possible temporal sequences of the random force. Eqs. (A1-2) and (A1-3) mean that the force $R(t)$ has the properties of Gaussian white noise. The Langevin equation approach tells us that the diffusion constant D is related to the frictional constant c and the strength of the thermal fluctuations in this system (i.e., the effective temperature for the present equation of motion, Eq.(A1-1)) as follows:

$$D = \frac{\gamma^2 H_E}{M_{\text{Fe}}} c k_B T_{\text{eff}}, \quad (\text{A1-4})$$

where k_B is the Boltzmann constant and T_{eff} is the effective temperature of the system. If the Langevin approach is applied to the microscopic LLG equations^{123,135}, which describes the motion of each spin in a large system, T_{eff} is equal to the real temperature T . The parameter D can be straightforwardly

related to the temperature T . On the other hand, if a mean-field approximation is applied, the microscopic LLG equations reduce for example to the sine-Gordon equation and thus loses microscopic information. In this case, it is difficult to determine the quantitative relation between D and T . Therefore, in this work, we should consider the effective temperature T_{eff} as a fitting parameter that takes the effect of thermal fluctuations into account (in the present notation, the dimension of T_{eff} is temperature per volume).

Secondly, when thermal fluctuations are considered and $\mathbf{M}$ is regarded as a local mesoscopic magnetization (that is, it is not the net magnetization of the whole considered volume), we also expect that the dynamics of each local $\mathbf{M}$ is affected by the other mesoscopic magnetizations around the local $\mathbf{M}$. Hence, we should introduce an additional mean-field-like potential on the top of the original mean-field potential energy W . This additional term should change as a function of the ensemble average $\langle \mathbf{M}(t) \rangle$ and is considered necessary, because W is the mean-field potential at the equilibrium state and does not include the effects of mesoscopic magnetizations with strong fluctuations around the local $\mathbf{M}$. It is reasonable that such an additional potential takes the form of an effective magnetic field B_C as a function of $\langle \theta(t) \rangle$. The equation of motion for θ including both thermal fluctuations and this additional phenomenological potential is given by

$$\begin{aligned} \ddot{\theta} + c\dot{\theta} = & -\chi \sin\theta (B_{\text{THz}}^{\text{NF}}(t) + B_{\text{DC}} + B_C(\langle \theta \rangle)) \\ & -a \sin\theta \cos\theta (\sin^2\theta + b) \\ & + 2\gamma B_{\text{THz}}^{\text{NF}}(t) \dot{\phi} \cos\theta \sin\theta + \gamma \dot{B}_{\text{THz}}^{\text{NF}}(t) \phi \cos\theta \sin\theta + R(t). \end{aligned} \quad (\text{A1-5})$$

The solution to this equation describes the dynamics of a specific local spin ensemble with a magnetization angle θ , and each ensemble has a different $R(t)$. The analytical expression for the effective magnetic field $B_C(\langle \theta \rangle)$ under the given conditions is not unique because several different types of expressions can be considered physically reasonable, but here we consider the following form:

$$B_C(\langle\theta\rangle) = \frac{B_{c0}}{2} \left\{ \xi \left[\cos \left(\pi \frac{\langle\theta\rangle - \theta_L}{\frac{\pi}{2} - \theta_L} \right) + 1 \right] \Theta \left(\frac{\pi}{2} - \langle\theta\rangle \right) \Theta \left(\langle\theta\rangle + \frac{\pi}{2} - 2\theta_L \right) \right. \\ \left. - \frac{B_{c0}}{2} \left\{ \left[\cos \left(\pi \frac{\langle\theta\rangle - \theta_R}{\theta_R - \frac{\pi}{2}} \right) + 1 \right] \Theta \left(\langle\theta\rangle - \frac{\pi}{2} \right) \Theta \left(2\theta_R - \frac{\pi}{2} - \langle\theta\rangle \right) \right\} \right\}, \quad (A1-6)$$

$$\Theta(x) = \begin{cases} 1 & (x \geq 0) \\ 0 & (x < 0) \end{cases}. \quad (A1-7)$$

B_{c0} and ξ are phenomenological parameters: B_{c0} is the strength of the effective magnetic field and ξ is the ratio of the strength of the effective magnetic field around the potential minimum at $\theta = \theta_L$ to that at $\theta = \theta_R$ ($\theta_L < \theta_R$). This function has the following properties: (i) If the average value $\langle\theta(t)\rangle$ is located around the left (right) minimum, the effective magnetic field makes it easier for a local magnetization angle θ to be located at the left (right) minimum too. (ii) B_C for $\langle\theta\rangle = \pi/2$ is zero, and $B_C(\langle\theta\rangle) > 0$ for $\langle\theta\rangle < \pi/2$ while $B_C(\langle\theta\rangle) < 0$ for $\langle\theta\rangle > \pi/2$ because B_C plays the role of a bias magnetic field. (iii) At the initial equilibrium state before pumping, $W(\theta_L) < W(\theta_R)$ due to the static magnetic field B_{DC} . In other words, a “force” that traps $\langle\theta\rangle$ around θ_L is already contained in the original potential W . Therefore, the additional potential should enhance the trapping of the magnetization angle θ around θ_R , rather than around θ_L . This is satisfied by $0 \leq \xi \leq 1$. (iv) B_C is a continuous function of $\langle\theta\rangle$. The parameters used in this section are shown in Table A1.

Table A1 | The parameters used in this section.

Parameter	Value
$k_B T_{\text{eff}}$	$1.4 \times 10^{-6} \text{ J/cm}^3$
B_{c0}	0.002 T
ξ	0.54

A2. Model of Kapitza pendulum

The Kapitza pendulum is a rigid pendulum of length l , where the point of suspension periodically oscillates along the vertical direction (regarded as the external driving force), as shown in Fig. A1. The coordinate of the ball of the Kapitza pendulum is given by¹²⁰,

$$x = l\sin\theta, \quad (\text{A2-1})$$

$$y = l\cos\theta + A\cos\omega t, \quad (\text{A2-2})$$

where ω and A are the oscillation frequency and amplitude, respectively. The Lagrangian is given by,

$$\begin{aligned} \mathcal{L} &= \frac{m}{2}(\dot{x}^2 + \dot{y}^2) - mgy \\ &= \frac{ml^2}{2}\left(\dot{\theta}^2 + \frac{2A\omega}{l}\sin\omega t\dot{\theta}\sin\theta\right) - ml^2\omega_0^2\cos\theta, \end{aligned} \quad (\text{A2-3})$$

where ω_0 is equal to $\sqrt{g/l}$, m is the mass of the ball and g is the gravitational acceleration. The motion equation is given by the Euler-Lagrange equation,

$$\ddot{\theta} + c\dot{\theta} = \omega_0^2\sin\theta - \frac{A\omega^2}{l}\cos\omega t\sin\theta, \quad (\text{A2-4})$$

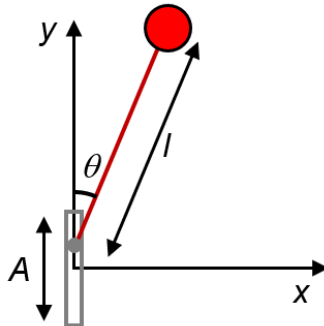


Figure A1. Schematic of Kapitza pendulum. The point of suspension periodically oscillates along the rail with the length of A .

where c is the damping factor. Eq. (A2-4) has the same form of external driving force with Eq. (5-14) which is proportional to $\cos\omega t \sin\theta$. When the oscillation frequency ω of the external driving force is much higher than the intrinsic frequency ω_0 of the pendulum due to gravity, the motion of θ can be decomposed into two components: a slow motion determined by the intrinsic potential energy, and a fast motion that is directly related to the external driving force. We obtain,

$$\theta = \theta_{\text{fast}} + \theta_{\text{slow}}. \quad (\text{A2-5})$$

Hereafter, we consider the high-frequency regime where $\omega \gg c, \omega_0$ holds, and assume that the magnitude of θ_{fast} is small, i.e., $|\theta_{\text{fast}}| \ll 1$. By using an expansion in powers of θ_{fast} , we derive the following approximate equations of motion:

$$\ddot{\theta}_{\text{fast}} + c\dot{\theta}_{\text{fast}} = \omega_0^2 \cos\theta_{\text{slow}} \theta_{\text{fast}} - \frac{A\omega^2}{l} \cos\omega t \sin\theta_{\text{slow}}, \quad (\text{A2-6})$$

$$\begin{aligned} \ddot{\theta}_{\text{slow}} + c\dot{\theta}_{\text{slow}} = & \omega_0^2 \sin\theta_{\text{slow}} \\ & - \frac{A\omega^2}{l} \cos\theta_{\text{slow}} \langle \cos\omega t \theta_{\text{fast}} \rangle_{\tau}. \end{aligned} \quad (\text{A2-7})$$

Here, $\langle \cdots \rangle_{\tau} = 1/\tau \int_t^{t+\tau} d\tau \cdots$ is the temporal average over a single oscillation period, $\tau = 2\pi/\omega$. θ_{fast} follows the forced oscillation of the external driving force and can be solved,

$$\theta_{\text{fast}} \approx \frac{A}{l} \cos\omega t \sin\theta_{\text{slow}}. \quad (\text{A2-8})$$

By substituting Eq. (A2-8) for θ_{fast} into Eq. (A2-7), the equation of motion for θ_{slow} can be rewritten,

$$\ddot{\theta}_{\text{slow}} + c\dot{\theta}_{\text{slow}} = \omega_0^2 \sin\theta_{\text{slow}} - \frac{A^2\omega^2}{4l^2} \sin 2\theta_{\text{slow}}. \quad (\text{A2-9})$$

The effective potential energy for θ_{slow} is given by the integration of terms on the right-hand side of Eq. (A2-9), as shown in Eq. (A2-10):

$$W_{\text{eff}} = \omega_0^2 \cos\theta_{\text{slow}} + \frac{A^2\omega^2}{4l^2} \sin^2\theta_{\text{slow}}. \quad (\text{A2-10})$$

The effective potential energy is consistent with the result of the Floquet-magnus expansion¹²⁰, indicating the Kapitza pendulum is a classical example of the Floquet engineering.

To visualize the shapes of the effective potential energies of Kapitza pendulum ($W_{\text{eff,p}}$) and the q-FM mode ($W_{\text{eff,s}}$), we rewrite Eqs. (A2-10) and (5-23),

$$W_{\text{eff,p}} = W_{0,\text{p}} + A_{\text{p}} \sin^2\theta_{\text{slow}}, \quad (\text{A2-11})$$

$$W_{0,\text{p}} = \cos\theta_{\text{slow}} \quad (\text{A2-12})$$

$$W_{\text{eff,s}} = W_{0,\text{s}} + A_{\text{s}} \sin^2\theta_{\text{slow}}, \quad (\text{A2-13})$$

$$W_{0,\text{s}} = \frac{-1.5\sin^2\theta_{\text{slow}} + \sin^4\theta_{\text{slow}}}{0.28125} + 1. \quad (\text{A2-14})$$

Here, $W_{0,\text{p}}$ and $W_{0,\text{s}}$ (315 K) are the static terms. A_{p} and A_{s} refer to the relative strengths of the additional terms. The effective potential energies are shown in Fig. A2. If the external driving forces were strong enough, the potential energies would exhibit minima at 0 and $\pm 180^\circ$ for both Kapitza pendulum and the q-FM mode, because the additional terms are proportional to $\sin^2\theta_{\text{slow}}$. However, due to the different forms of the static terms, the developments of the potential minima are different. For Kapitza pendulum, due to gravity, the static term has a minimum at $\pm 180^\circ$. As A_{p} increases, new potential minimum suddenly appears at 0° . In contrast, for the q-FM mode, as A_{s} increases, the initial potential minima shift towards 0° and $\pm 180^\circ$ gradually.

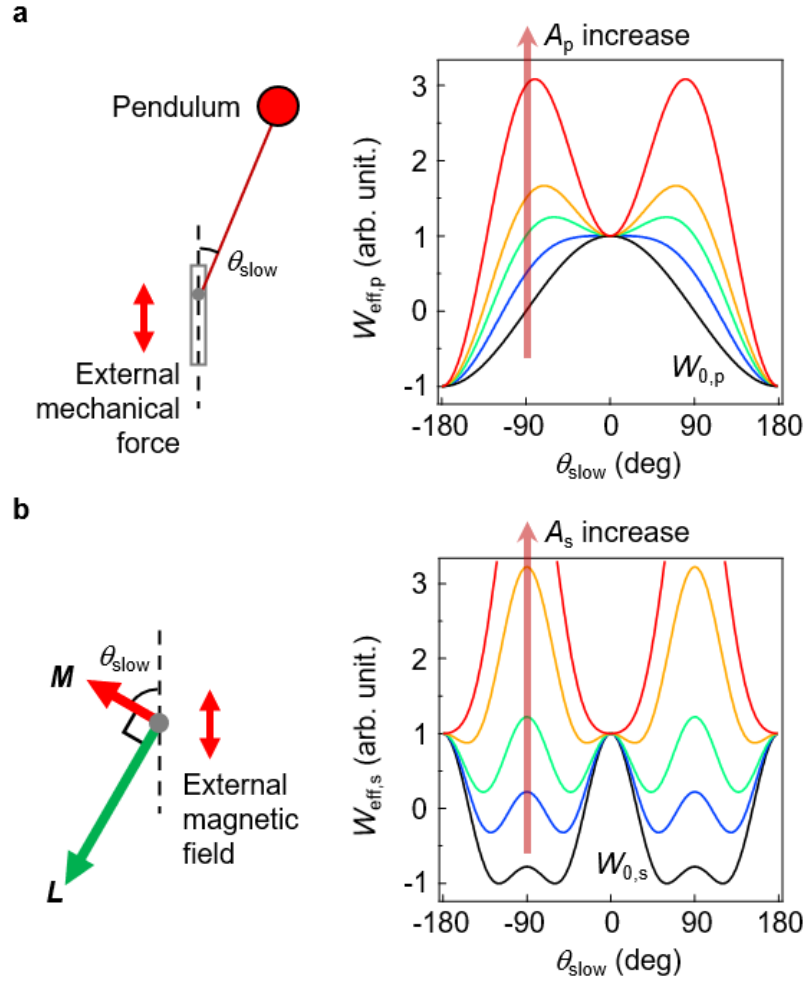


Figure A2. Comparison between the effective potential energy of Kapitza pendulum (a) and q-FM mode (b).

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