

**Study On Mid-Infrared Free Electron Laser-Driven Specific
Phonon-Assisted Energy Transitions: Hyper-Raman
Scattering and Antiferromagnetic Domain Dynamics**

2026

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A thesis for the degree of Ph.D.

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2026

Abstract

Controlling material properties on ultrafast time scales with minimal energy dissipation is a central challenge in the development of next-generation information and energy technologies, particularly for correlated systems in which charge, spin, orbital, and lattice degrees of freedom are strongly interconnected. Resonant excitation of lattice vibrations has emerged as a particularly attractive route, as mid-infrared photons can be coupled to zone-center optical phonons and steer electronic and magnetic order through nonlinear processes, without substantial electronic heating, thereby overcoming the intrinsic speed and dissipation limitations of field- and current-drive approaches. Motivated by this concept, this work establishes a mid-infrared free-electron laser (MIR-FEL) as a versatile source for selective excitation of phonon modes in strongly correlated oxides. Combined with the MIR-FEL, synchronized nanosecond and picosecond probe lasers are used to implement pump-probe experimental configurations and elucidate how specific phonons facilitate energy-transfer processes, with particular focus on hyper-Raman scattering and antiferromagnetic domain-recovery dynamics. In the first part of this study, a Strontium Titanate (SrTiO_3) single crystal is irradiated by tuning the MIR-FEL pulses to $12.5\text{ }\mu\text{m}$, which resonates with the LO3 phonon mode. Owing to the centrosymmetric perovskite structure, this phonon mode is infrared-active but Raman-inactive. However, it becomes accessible through a second-order nonlinear Raman process. Therefore, hyper-Raman spectroscopy, which is governed by the hyperpolarizability tensor, is employed to overcome the Raman selection rule constraints. By detecting the anti-Stokes hyper-Raman scattering spectrum at 5 K, where thermal excitations are suppressed, the selective excitation of the LO3 phonon mode was confirmed. The second part of this study focuses on how different resonant phonon excitations influence changes in antiferromagnetic order in bulk Nickel Oxide (NiO). Time and temperature-resolved magneto-optical linear birefringence microscopy in transmission geometry is employed to visualize magnetic domain patterns, while the MIR-FEL is tuned to the 2TO ($13.5\text{ }\mu\text{m}$) and LO ($17.15\text{ }\mu\text{m}$) phonon modes, which exhibit strong but opposing spin-phonon coupling conditions. Phonon mode selectivity and temperature dependence have been confirmed as the magnetic domain reconfigurations induced by 2TO phonons persist for milliseconds and exhibit thermally retarded recovery as temperature approaches the Néel temperature of NiO, whereas LO phonon-induced changes relax within a microsecond range and recover faster with elevated temperature.

Acknowledgement

I would like to express my deepest and most sincere gratitude to my supervisor, **Ohgaki sensei**. He continuously encouraged me to grow as a researcher and as a person. Despite my shortcomings and limited experience in many areas, he remained patient and supportive, consistently providing constructive advice and steady encouragement. His care and consideration went beyond academics, and I am profoundly grateful for the environment of understanding and support he created for me.

I am truly grateful to **Zen sensei**, as none of this research would have been possible without him. His insightful discussions, clear guidance, and generous support played a crucial role in shaping this work and helping me overcome many challenges along the way.

I would also like to thank **Jordi sensei**, whose kindness and thoughtful discussions and conversations provided perspective and encouragement, making this journey less stressful.

I sincerely appreciate **Nagaya-san**, our wonderful assistant administrative staff, whose kind support has greatly eased my worries about administrative procedures from the very day I arrived in Japan.

Finally, I would like to thank my family members and friends who have stood by me with unwavering emotional support throughout this long and challenging journey. Their encouragement and understanding gave me the strength to keep going, especially through extremely tough times.

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List of abbreviations

DC	Direct current
THz	Terahertz
ISRS	Impulsive stimulated Raman scattering
IR	Infrared
AFM	Antiferromagnetic
TMO	Transition metal oxides
SrTiO ₃	Strontium Titanate
NiO	Nickel Oxide
LO	Longitudinal optical
TO	Transverse optical
2TO	Second-order transverse optical
2M	Second-order magnon
MIR-FEL	Mid-infrared free-electron laser
KU-FEL	Kyoto University Free-Electron Laser
T _c	Curie temperature
T _N	Néel temperature
MOKE	Magneto-optical Kerr effect
XMLD	X-ray magnetic linear dichroism
PEEM	Photoemission electron microscopy
SSIM	Structural similarity index measure
MSSIM	Mean structural similarity index measure

Chapter 1

Introduction

1.1. Overview

Controlling material properties with minimal energy consumption and on the shortest possible timescale remains an ultimate goal in modern materials science. Whether for data storage, logic devices, or low-power neuromorphic hardware, the trend is evident: lower energy consumption, faster response times, and reduced thermal dissipation are highly desirable. Traditional routes to switching and tuning order parameters, such as applying DC electric or magnetic fields, external stress, or heating and cooling through phase transitions, are simply too slow and energy-wasteful to satisfy the needs of next-generation technologies. Pioneering methods discovered in recent decades can act on shorter time scales with significantly less energy dissipation.^{1)–8)} One example is magnetoelectric control, in which materials with electric and magnetic orders are strongly coupled, allowing magnetization to be controlled by an electric field and vice versa.^{9)–11)} This magnetoelectric approach is promising for low-power, energy-efficient switching in future devices. However, even such conventional field-driven methods are limited by intrinsic speed constraints, so that the switching typically cannot proceed faster than nanoseconds due to the ramp-up time of the applied fields and associated dissipation.¹²⁾ Accordingly, identifying more efficient ways to rapidly control or manipulate the phases or states of matter has become a key challenge in developing advanced functional materials.

In recent years, ultrafast optics research has shown that femtosecond laser pulses can significantly reshape electronic, magnetic, and structural states on sub-picosecond time scales.^{3),12)–16)} However, many of the ultrafast optics approaches that depend on strongly exciting electronic degrees of freedom and electronic heating not only limit the energy

efficiency of control methods but also tend to erase the delicate quantum or correlated states one may wish to manipulate.^{17)–20)} Against this backdrop, phononic control, which involves steering material properties through tailored lattice vibrations, has emerged as a particularly attractive alternative.^{1),2),6),13),14),21)–24)} Instead of using electrons as the primary handle, if the light pulse is tuned to resonate with a particular lattice vibrational mode (phonon mode), the energy couples into coherent atomic motion rather than random heating of the crystal. Through anharmonic couplings (phonon-phonon interactions), spin-phonon interactions, or electron-phonon interactions, the resonantly induced phonons can modify electronic bandwidths, exchange interactions, and create transient configurations that are not present in equilibrium. Phononic control is particularly effective in strongly correlated materials, where even slight lattice distortions can significantly change electronic transitions and exchange interactions. Hence, this offers a promising route to non-thermal, energy-efficient ultrafast control, enabling access to new phases or reconfigurations while injecting far less entropy than conventional methods.

1.2. Laser-driven phonon excitations

When electromagnetic radiation (a laser) interacts with the crystal, energy can be absorbed and transferred to the lattice through several distinct mechanisms, primarily determined by the photon energy relative to the material's electronic bandgap and available phonon frequencies. The mechanisms include direct absorption, indirect absorption via electronic carriers (heating and scattering), and nonlinear optical processes such as Raman scattering. For a direct and specific absorption to occur, the light must have a frequency that matches the electric dipole carrying phonon mode frequencies, and a pulse with a duration shorter than the phonon lifetime.^{6),25)} This process creates coherent phonons, collective phase-locked macroscopic oscillations, without necessarily interacting with the electronic systems.^{25),26)} These are the primary drivers of nonlinear phonons, in which their large-amplitude vibrations induce

transient modifications to the crystal structure, leading to phase transitions and changes in material properties. Nonetheless, directly exciting coherent phonons can be challenging, primarily due to the need for terahertz (THz) technology. This highlights the importance of indirect and nonlinear pathways. When the laser photon energy exceeds the material's electronic bandgap (for the case with visible or near-infrared lasers), energy is initially absorbed by electrons, which then transition to excited states. These then rapidly relax by transferring energy to the lattice on a picosecond timescale. This process is often known as impulsive stimulated Raman scattering (ISRS), where electronic-state excitations trigger indirect phonon excitation through electron-phonon interaction.^{27),28)} Under ultrafast excitation conditions, ISRS offers a pathway to generate coherent phonons while minimizing net electronic heating via the electron-phonon coupling, even if the incoming photons are not resonant with phonon energies.

Beyond these linear mechanisms, truly nonlinear behavior emerges when an intense mid-infrared (IR) or THz field is resonantly tuned to drive an IR-active phonon to larger amplitudes.^{6),24),29)–32)} In this regime, strong anharmonic coupling between the resonantly driven mode and other, typically lower-frequency, Raman-active modes leads to coherent reshaping of the crystal structure via nonlinear energy transfer. The resulting lattice distortions can transiently stabilize or enhance ordered phases, shift transition temperatures, or induce entirely new metastable configurations that are not accessible under equilibrium conditions.

1.2.1. Nonlinear phononic manipulation of material properties

Nonlinear phononic manipulation involves changes triggered by tailored laser-driven phonons to introduce complex structural modifications and achieve striking, unexpected alterations in material properties. In recent years, several studies have emerged confirming the capabilities of phononic manipulation. From first-principles theory calculations, M. Fechner et al. found that driving an IR-active polar A_{1g} mode (~ 17 THz) in Cr_2O_3 alters the Cr- Cr distance and, hence, the exchange coupling, creating a transient antiferromagnetic (AFM) state during the phonon excitation.²⁾ From the selective IR numerical stimulation of the narrow phonon bands in crystalline α -RDX, it has been found that the excitation at the molecular translation mode ($\sim 22.74 \text{ cm}^{-1}$) can reduce the overall thermal conductivity by 12.46 % and the excitation at the CH_2 twisting and rocking mode ($\sim 1140.67 \text{ cm}^{-1}$) can increase the thermal conductivity by 144.07 %.³³⁾ Theoretical research on tensorial spin-phonon relaxation by Dmitriev et al found that only a few vibrational modes significantly influence the spin coherence time, while a single phonon mode is responsible for the majority of transverse relaxation.³⁴⁾ Rini et al. observed an insulator-to-metal phase transition, where a metastable metallic phase results from the resonant excitation Mn-O phonon mode ($17.5 \text{ }\mu\text{m}$) via direct mid-IR laser irradiation in the strongly correlated material $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.³⁵⁾ Similarly, Forst et al. experimentally demonstrated the magnetic order control via the coherent optical excitation of the Mn-O stretching vibration in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$.³⁶⁾ D. Afanasiev et al. also demonstrated an ultrafast spin reorientation and metastable transition from AFM to a weak-ferromagnetic state in DyFeO_3 through resonant excitation of an IR-active B_u phonon mode (~ 17 THz) associated with the Fe-O stretching bond.¹³⁾ These prior observations outline that not all, but only certain phonon modes, primarily affect the system properties, emphasizing the importance of choosing modes selectively.

1.3. Materials of interest (Strongly correlated materials)

As the name “strongly correlated materials” indicates, the degrees of freedom (charge, spins, orbital, and lattice) strongly interact with each other and significantly influence the material properties. Consequently, phonons in these materials profoundly affect and are affected by electronic correlations, resulting in unusual behaviours such as lattice distortions associated with magnetic or electronic transitions. Transition-metal oxides (TMOs) are ideal examples of strongly correlated materials. Their partially filled 3d orbitals, contributed by the transition-metal atoms, result in strong Coulomb repulsion, making electronic correlations the dominant factor.^{37),38)} Such correlations give rise to a wealth of intriguing electronic and thermodynamic properties, as well as diverse phenomena such as metal-insulator transitions, colossal magnetoresistance, multiferroicity, and high-temperature superconductivity.³⁷⁾ As a result, TMOs serve as excellent platforms for studying phononic manipulation, given their lattice distortions and phonon modes closely linked to the system.

1.3.1. Strontium Titanate (SrTiO₃)

SrTiO₃ is one of the classic TMOs, exhibiting complex electronic behavior and a wide variety of quantum states.^{39)–42)} SrTiO₃ has attracted interest due to its unique ability to enhance the superconducting transition temperature, which is closely related to its complex phonon dynamics and strong electron-phonon interactions.^{43)–46)} In recent studies, a remarkable increase in the superconducting transition temperature (T_c) from 8 K to 40–109 K has been observed for FeSe monolayers grown on SrTiO₃ substrates.⁴⁷⁾ SrTiO₃ was found to play a crucial role in this T_c increment as the TiO₂-terminated face of SrTiO₃ prevents the FeSe layer from undergoing a structural phase transition and enables an anti-ferromagnetic ground state of FeSe. This enabled specific electron-phonon coupling channels within the FeSe monolayer that are prevented by symmetry in the non-magnetic phase. Accordingly, the magnetic and interfacial electron-phonon interactions at the FeSe/SrTiO₃ interface are found to be the key

factor, rather than strain or dielectric constant, in achieving T_c enhancement. Out of all phonon modes in SrTiO_3 , the LO3 mode shows the strongest coupling with electrons.⁴⁸⁾ Additionally, six out of seven available phonon modes of SrTiO_3 are Raman forbidden, making it interesting and challenging to investigate the phonon-induced dynamics using conventional Raman techniques. (Details of SrTiO_3 crystal characteristics and phonon modes are presented in Section 4.2, Chapter 4)

1.3.2. Nickel Oxide (NiO)

NiO is also a prototypical TMO and one of the most widely studied strongly correlated materials, which adopts a collinear type-II antiferromagnetic (AFM) order at room temperature. The fundamental challenge for AFM material control is that they carry no net magnetic moment, and therefore, conventional manipulation with an external magnetic field, widely used for ferromagnets, is ineffective. While current-induced switching approaches have shown progress in certain AFM materials, they still lack universality and often involve significant heat dissipation.^{49)–51)} As a result, controlling antiferromagnetic order requires alternative stimuli. The recent work by Stremoukhov et al. demonstrated that coherent phonon excitation can be a promising control of AFM order in NiO. By illuminating NiO with narrow-band mid-IR pulses tuned across the phonon spectrum (12.5 to 30 μm , 800 to 330 cm^{-1}), resonant excitation of LO and 2TO phonon modes in NiO was found to cause significant, temporary shifts in magnetic domains. In contrast, excitation at the strongly absorbing IR-active TO phonon results in a minimal effect response.²¹⁾ This indicates that certain phonon modes in NiO strongly couple differently to the spin states and can allow targeted modification of AFM order via phonons, whereas other mechanisms fail due to symmetry and magnetic compensation. (Details of NiO characteristics, spin-phonon coupling conditions, and AFM domains are presented in Section 5.2, Chapter 5)

1.4. Motivation and objective

The mid-IR excitation of phonon modes has emerged as a particularly promising approach because it can directly couple to the lattice and induce non-thermal structural and electronic transitions through nonlinear phonons. However, accessing and controlling specific phonon modes remain technically challenging. Many of the most functionally relevant modes are Raman-forbidden or weakly coupled under conventional optical probing conditions. Overcoming symmetry selection rules to excite such phonons selectively is a critical step toward advancing phononic control. In this context, two key challenges motivate the present work. First, most optical phonon modes in SrTiO_3 are forbidden in the first-order Raman process, yet they significantly influence the superconducting transition temperature by coupling with electrons. Second, for AFM NiO , the absence of net magnetization makes conventional field-based control inefficient, even though it can offer intrinsically faster dynamics than traditional ferromagnetic devices.

The central goal of this study is to establish mid-IR laser-driven selective phonon excitation using the mid-infrared free-electron laser (MIR-FEL) from the Kyoto University Free-Electron Laser facility (KU-FEL), and to investigate how phonon-induced changes in material properties are achieved through phonon-assisted energy transition processes, such as electron-phonon and spin-phonon interactions. The specific objectives are

1. To develop and characterize the MIR-FEL pump and probe laser configurations for resonant phonon excitations, including precise timing synchronization.
2. To demonstrate selective excitation and detection of a specific target Raman-forbidden phonon mode in SrTiO_3 driven by MIR-FEL irradiation, enabling direct access to phonon symmetries that govern its functional properties.

3. To investigate the temporal evolution of phonon-driven AFM domain dynamics in NiO, examining the impact of phonons on magnetic reconfigurations.

By achieving these objectives, this study aims to provide a coherent picture of the MIR-FEL-driven specific phonon-assisted energy transitions and establish a foundation for phonon-engineered control of strongly correlated materials.

1.5. Outline of thesis

In Chapter 2, basic details about lattice vibrational modes, electron spins, and their various types are introduced. The concept of magnetic domains (groups of clusters with aligned spins) and methods to visualize them are discussed. Additionally, brief notes on how these quasiparticles interact and coexist with one another, such as phonon-phonon, electron-phonon, spin-phonon, and phonon-magnon interactions, are provided, along with how these phenomena influence material properties. The chapter also explains how phonons assist in electron excitation and spin alignment processes.

In Chapter 3, the experimental setup for inducing phonon excitations using the mid-infrared free-electron laser (MIR-FEL) at Kyoto University's KU-FEL facility is described. This section includes details about the MIR-FEL's characteristics and pulse structures. Since our experiments involve probe lasers for direct observation, precise synchronization and timing control of both pump and probe lasers are crucial. We also explain how these adjustments are made and present the unforeseen outcomes.

In Chapter 4, we discussed our observation of the selective excitation of a Raman-forbidden phonon mode. MIR-FEL has already demonstrated the ability to excite and verify IR-active, IR-inactive, and Raman-active phonon modes. However, selective excitation of Raman-inactive modes has not yet been achieved. To address this, we implemented synchronized

pump-probe laser timing to perform selective excitation and confirmed our attempt using hyper-Raman spectroscopy.

In Chapter 5, we discuss our observations of how phonon-induced magnetism in NiO changes over time after resonant excitation from irradiation by MIR-FEL. We captured antiferromagnetic domain images both with and without MIR-FEL irradiation, adjusting the probe delay up to 20 ms, and analysed the images using the structural similarity index measure. This allowed us to determine the recovery dynamics of AFM domains following resonant phonon excitation.

In Chapter 6, we further examined how different phonon modes and temperature influence phonon-induced dynamics in the AFM domains of NiO. We compared results from 2TO and LO phonon excitations as the temperature was raised from Room temperature to 532 K. This comparison illustrates how the AFM domain pattern varies depending on the specific phonon mode and thermal environment.

Lastly, in Chapter 7, we summarized and concluded our observations, discussed the future perspectives, and explored the potential applications of our study.

Chapter 2

Strongly correlated systems

2.1. Phonons

Phonons, quantized collective vibrations of a crystal lattice, are one of the fundamental quantum excitations in atomic solids. They govern the nature of materials, from thermal transport and structural stability to various coupling-driven electronic, optical, and magnetic behaviours. Microscopically, phonons emerge from atomic interactions and crystal lattice symmetry, and their dispersion relations encode fundamental information about interatomic forces and practical constraints on heat and sound propagation. Beyond these, phonons also act as active mediators of interactions with other quasiparticles, such as electrons and spins, enabling modifications to phase transitions and corresponding parameters.

Microscopically, phonons emerge from the harmonic interactions of atoms in the crystal. Modeling atoms as masses connected by interatomic springs yields plane-wave normal modes for the lattice vibrations, and each such mode at wavevector k is a collective oscillation of every atom in the crystal. In quantum terms, each phonon carries discrete energy $E = \hbar\omega$, and momentum $p = \hbar k$, where $\hbar$ is the reduced Planck constant, ω is the angular frequency, and k is the wave vector. Phonons possess both group velocity and phase velocity. The group velocity describes the velocity at which energy propagates with the movement of phonons, while the phase velocity represents the velocity of the wave itself. These velocities are crucial for information on how phonons transport energy and momentum through the crystal lattice.

2.1.1. Types of phonons

Phonons can be classified into two categories: acoustic phonons and optical phonons. Acoustic phonons are low-frequency vibrational modes of the crystal lattice, corresponding to in-phase oscillation of atoms, and are responsible for the propagation of sound waves. The velocity of the acoustic phonons determines the speed of sound in materials. Optical phonons are high-frequency modes involving out-of-phase motions of different types of atoms in the unit cells. They have a non-zero frequency at the Brillouin zone center (Γ -point), unlike the acoustic phonons. Optical phonons interact with electromagnetic radiation through infrared absorption, with their infrared activity determined by the symmetry of the crystal lattice. In centrosymmetric crystals, these phonons are either infrared or Raman-active. Phonons can be further categorized into longitudinal and transverse modes depending on the direction of wave propagation. They are often abbreviated as LA and TA for longitudinal acoustic and transverse acoustic phonons, and as LO and TO for longitudinal optical and transverse optical phonons.

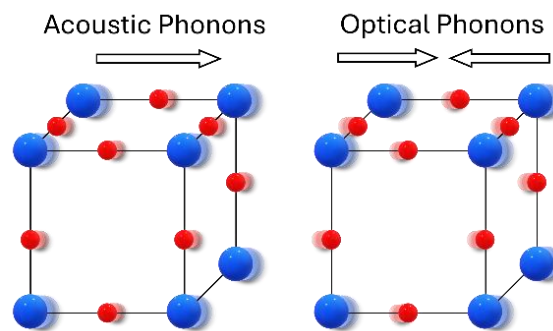


Figure 2.1. Acoustic and optical phonons in a crystal lattice with two different atoms

2.1.2. Vibrational spectroscopy

Conventional approaches to analyzing vibrational modes, such as phonons, involve infrared and Raman spectroscopy techniques. A vibrational mode that can absorb infrared light is denoted as an infrared-active mode. Infrared absorption occurs due to a change in the dipole moment, and therefore, materials that do not display a change in dipole moment do not exhibit

infrared absorption. Optical phonon modes exhibiting a change in dipole moment are known to be infrared-active. However, since electromagnetic waves are transverse waves, only the TO modes are observable in infrared spectroscopy when infrared light is incident perpendicular to the sample surface. Therefore, LO modes will only be observable when the light is incident at an oblique angle to the material surface. In contrast, a vibrational mode that exhibits a change in polarization as it absorbs or emits energy due to the incident photon is known as a Raman-active mode. Infrared and Raman spectroscopy are complementary to each other as they follow the mutual exclusion principle. This principle states that in a centrosymmetric crystal, a phonon mode can be either infrared-active or Raman-active, but not both simultaneously. Raman spectroscopy has a slight advantage over infrared spectroscopy due to its narrower bandwidth, allowing for easier access to different modes in the sample mixture. However, neither conventional Raman nor infrared spectroscopy is sensitive to acoustic phonons, as they are located at the Γ -point and have zero energy.⁵²⁾ Instead, other techniques, such as Brillouin light scattering spectroscopy, terahertz time-domain spectroscopy, and laser Doppler vibrometry, can be implemented to detect acoustic phonon modes.⁵³⁾

2.1.2.1. Raman scattering spectroscopy

This section further introduces Raman scattering spectroscopy, as our main focus is on optical phonon modes. In terms of classical expression, the energy $\vec{E}_i$ of light that interacts with a molecule can be expressed as

$$\vec{E}_i = E_i \vec{e} \cos(2\pi\nu_i t) \quad \text{Eq. (2.1)}$$

E_i represents the amplitude and polarization of the incident electric field, $\vec{e}$ is the unit vector, ν_i is the frequency of the light wave at time t . And irradiating a molecule with light wave, it alters the distribution of the electron, which induces dipole moment $\vec{P}$, and can be described as

$$\vec{P} = \alpha \vec{E}_i \quad \text{Eq. (2.2)}$$

where α refers to the second-rank polarizability tensor.

In addition, a molecule vibrates periodically, and α is expressed as

$$\alpha = \alpha_0 + \alpha_1 \cos (2\pi\nu_p t) \quad \text{Eq. (2.3)}$$

, where α_0 is the component independent of time and α_1 is the time-dependent component, ν_p is the vibrational frequency.

And therefore,

$$\begin{aligned} \vec{P} &= \alpha \vec{E}_i \\ &= \alpha E_i \vec{e} \cos (2\pi\nu_i t) \\ &= [\alpha_0 + \alpha_1 \cos (2\pi\nu_p t)] E_i \vec{e} \cos (2\pi\nu_i t) \\ \vec{P} &= E_i \vec{e} [\alpha_0 \cos (2\pi\nu_i t) + \alpha_1 \cos (2\pi\nu_i t) \cos (2\pi\nu_p t)] \end{aligned}$$

(Using the equation $\cos(x)\cos(y) = \frac{1}{2} \cos (x-y) + \frac{1}{2} \cos (x+y)$)

$$\begin{aligned} \vec{P} &= E_i \vec{e} [\alpha_0 \cos (2\pi\nu_i t) + \frac{1}{2} \alpha_1 \cos (2\pi\nu_i t - 2\pi\nu_p t) + \frac{1}{2} \alpha_1 \cos (2\pi\nu_i t + 2\pi\nu_p t)] \\ \vec{P} &= E_i \vec{e} [\alpha_0 \cos (2\pi\nu_i t) + \frac{1}{2} \alpha_1 \cos (2\pi(\nu_p - \nu_i) t) + \frac{1}{2} \alpha_1 \cos (2\pi(\nu_p + \nu_i) t)] \quad \text{Eq. (2.4)} \end{aligned}$$

The first term in this equation represents elastic Rayleigh scattering, the second term represents Stokes-Raman scattering, and the third term represents anti-Stokes Raman scattering.

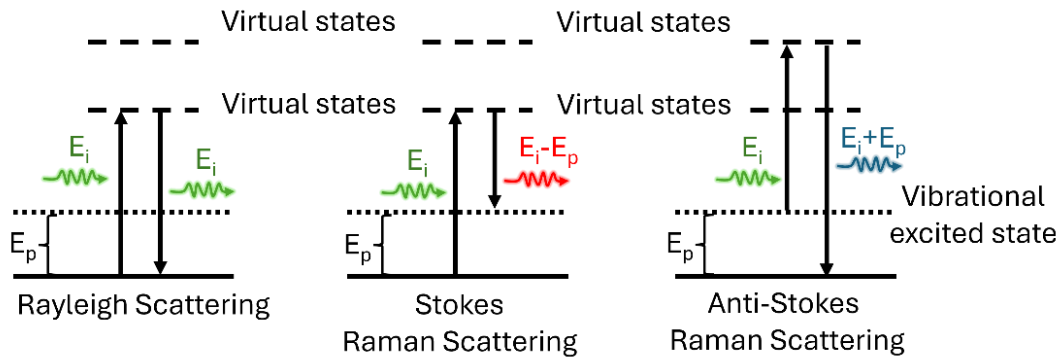


Figure 2.2. Energy transfer process in Rayleigh, Stokes, and anti-Stokes Raman scattering

If the incident light/photon interacts with a crystal lattice/molecule, it can either scatter elastically or inelastically. In elastic scattering, no vibrational assistance throughout the process; the same energy as the incident light is scattered. This process is known as Rayleigh scattering. In inelastic scattering, the energy transfer process involves lattice vibrations/phonons, which leads to Stokes and anti-Stokes Raman scattering processes. The mechanism of Stokes scattering involves a photon from the incident light exciting an electron from its ground state to an excited state. The excited electron then interacts and transmits energy to a phonon during its relaxation process. The energy released during its relaxation is less than the initial energy, as a portion of it is transferred to the phonon. For the anti-Stokes scattering process, an electron in the ground state is already excited to a vibrationally excited state by the interaction of a phonon. Then this electron is further excited to a higher energy level by the interaction of the incident light. Then, the excited electron releases energy, which is higher than the incident energy, as it relaxes back to the ground state. As a result, the Stokes scattering peaks appear at a lower energy level, while the anti-Stokes peaks appear at a higher energy level in the spectrum. In Raman scattering, the excited states resulting from the perturbation by the incident photon typically do not correspond to the system's electronic states and are usually denoted as virtual energy states. As the incident photon energy approaches the energy of the electronic states, the strength of the Raman effect increases. If the virtual energy

state finally matches the discrete electronic energy state of the system, the interaction is then described as resonance Raman scattering. Raman scattering spectroscopy has two types: linear and nonlinear. The above theoretical expressions apply to a linear Raman scattering process, where the intensity of the scattered light is directly proportional to the intensity of the incident light. Nonlinear Raman scattering includes resonance Raman scattering, stimulated Raman scattering, hyper-Raman scattering, etc.

2.2. Electron spins

At the atomic level, magnetism originates from two primary sources: (1) the orbital motion of electrons around the nucleus, μ_{orb} (orbital magnetic dipole moment), and (2) the intrinsic spins of electrons, μ_{spin} (spin magnetic dipole moment). These two factors combine to determine the overall magnetic moment of an atom or molecule, expressed as $\mu = \mu_{\text{orb}} + \mu_{\text{spin}}$. Usually, in materials with unpaired electrons, the spin magnetic moment is the main contributor.

2.2.1. Spin's exchange interactions and types of magnetisms

The exchange interaction is a fundamental quantum mechanical force that aligns electron spins in magnetic materials, arising from the Pauli Exclusion Principle. This principle states that no two identical particles with half-integer spins, such as electrons, can occupy the same quantum state simultaneously. Depending on the exchange interaction resulting from the material's electronic structure and atomic arrangements, different types of magnetism develop. The primary types include

- 1) Diamagnetism: This is a quantum-mechanical phenomenon present in all materials. It arises from changes in electron orbital motion induced by an external magnetic field, resulting in an opposing orbital magnetic moment, $-\mu_{\text{orb}}$, that weakly opposes the field.

- 2) Paramagnetism: This occurs in materials containing unpaired electrons that have permanent magnetic moments, resulting in randomly oriented spins. Unlike diamagnetism, these moments align when an external magnetic field is applied. However, in the case of paramagnetic materials, the exchange interaction between the aligned electron spins is much smaller than the thermal energy, i.e, the kinetic energy of the electrons. As a result, the stabilization of electron spin alignment by the external magnetic field will not persist after the field is removed.
- 3) Ferromagnetism: This is the strongest form of magnetism, where the exchange interaction aligns neighbouring electron spins parallel to each other. Here, the exchange interaction overcomes thermal randomization, and the spin alignment remains below the Curie temperature (T_c), making it difficult to demagnetize even after the external field is removed. Above T_c , the ferromagnets transition into paramagnetic states.
- 4) Antiferromagnetism: Antiferromagnetism occurs when the exchange interaction favours antiparallel alignments between the neighbouring spins. Here, the adjacent magnetic moments cancel out each other, and therefore, antiferromagnets exhibit zero net magnetization. Antiferromagnets also transition to paramagnetic states above the transition temperature known as the Néel temperature (T_N).
- 5) Ferrimagnetism: Ferrimagnetism combines features of ferromagnetism and antiferromagnetism, where neighbouring spins with unequal magnitude align antiparallelly, resulting in a net magnetization. This type of magnetism typically occurs in compounds with different magnetic ions occupying distinct crystallographic sites.

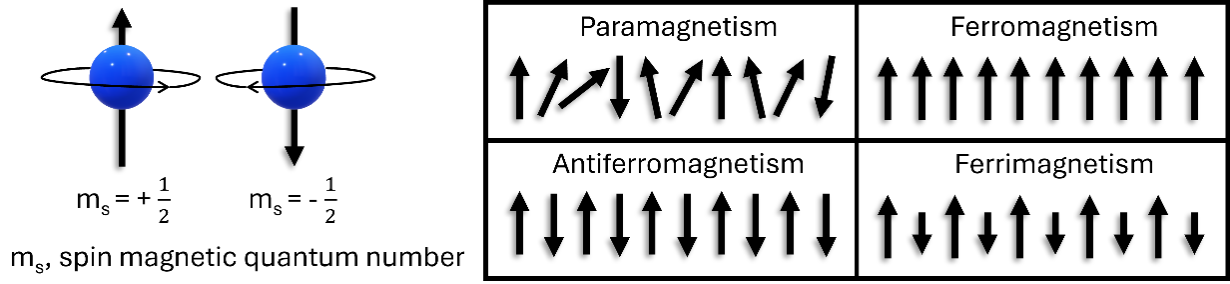


Figure 2.3. Electron spins and different types of magnetism

2.2.2. Magnetic domains

The microscopic spin alignments form regions with uniform spin orientations, resulting in complex configurations known as magnetic domains. The regions separating two different magnetic domains are also represented as domain walls. There exist two primary domain wall types shown in Figure 4: (1) Bloch wall, where the magnetization rotates about an axis normal to the domain wall plane, and (2) Néel wall, where the rotation is within the domain plane.⁵⁴⁾ In bulk ferromagnetic materials, Bloch walls are dominant, whereas in thin films, Néel walls are. Generally, the magnetic domains and domain walls form to minimize and stabilize the material's overall magnetoelastic energy at the macroscopic level. Domain formations and their configurations are governed by various energy contributions. These include (1) magnetic interaction energy between neighbouring alignments⁵⁵⁾ (2) magnetoelastic energy, which is coupled to the shape and dimension of the materials^{56),57)} (3) magneto-crystalline anisotropy energy due to the favour in spin alignment along specific crystallographic directions⁵⁸⁾. The sizes of the magnetic domains can vary drastically. The typical size range of a single magnetic domain in bulk materials is from ~ 1 to $100 \mu\text{m}$, whereas in thin films, it is up to tens of nanometers.^{59)–61)}

In AFM materials, an analogous domain concept applies, in which each domain has a uniform, staggered spin order defined by the orientation of the Néel vector. AFM domain walls form on cooling through the T_N , and are stable only if the magnetic anisotropy is sufficiently weak.⁶²⁾

In practice, AFM domain walls are typically pinned by lattice defects or strain fields.⁶²⁾ Imaging experiments on collinear AFMs have found predominantly Bloch-like 180° walls, with Néel-type walls appearing only when a strong in-plane anisotropy is present.⁶³⁾ Accordingly, AFM materials are found to be capable of hosting either Bloch or Néel walls, analogous to those in ferromagnets, despite lacking a net magnetization.

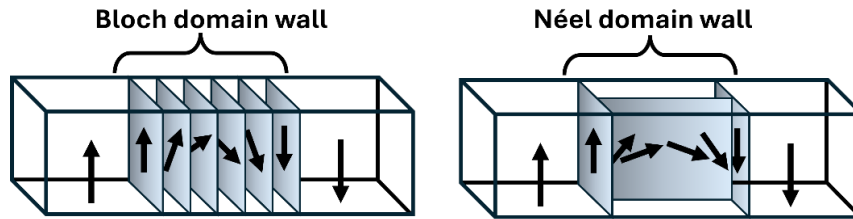


Figure 2.4. Two primary types of magnetic domain walls, Bloch domain wall (left) and Néel domain wall (right)

Magnetic domains can exhibit movements that underpin magnetization switching. Domains and domain walls are sensitive to and can be modulated by external fields, such as electric and magnetic fields, as well as environmental factors, including strains and temperature variations.^{64)–69)} Domain movements primarily occur through two mechanisms: (1) domain wall displacement and (2) domain rotation. When stimulated by an external electric or magnetic field, the domain walls move through the material, causing domains to grow or shrink. At low fields, domain walls move via thermally activated motions, and at high fields, they move viscously with speed proportional to the field, and the domain movement becomes oscillatory above the threshold field.^{68),70)} Domain rotations occur predominantly in strong fields or under substantial stress and optical manipulation, causing the internal spin orientation within a domain to rotate without domain wall movements.⁷¹⁾

Understanding magnetic domain dynamics is crucial for designing materials used in data storage, sensors, and other applications that rely on magnetic properties. To gain a thorough

understanding, visualizing magnetic domains is necessary. The next section discusses possible methods for visualizing AFM domain structures.

2.2.2.1. Magneto-optical birefringence

Imaging techniques for magnetic domains on the surfaces of ferrimagnets and ferromagnetic materials have been extensively developed over several decades. These primarily include methods based on the magneto-optical Kerr effect (MOKE).^{72),73)} The principle involves incident light reflecting off the magnetic surface, causing the polarization to rotate by an angle due to the interaction between the light and the surface's magnetic moment. Since the rotation depends on the direction and magnitude of the magnetization, changes in magnetic order can be simply derived from shifts in the polarization of the reflected light.

In contrast, imaging AFM domain patterns has always been more challenging, primarily due to their lack of a net magnetic moment. For non-collinear AFM materials, MOKE microscopy remains accessible, despite their small net magnetization.^{74)–77)} However, for collinear AFM materials with fully compensated spin alignments, the MOKE effect cannot be implemented due to the cancellation of sub-lattice magnetization. The imaging of AFM domains usually requires complex techniques such as X-ray magnetic linear dichroism (XMLD)^{78)–80)}, photoemission electron microscopy (PEEM)^{60),79),81)}, cryogenic magnetic force microscopy⁸¹⁾, and neutron diffraction.^{82)–84)} Among these, the PEEM based on XMLD effect is the most common technique used to study magnetic domains of AFM surfaces and thin films.^{75),80),85)–87)} However, XMLD-PEEM measurements require access to large synchrotron facilities and are difficult to incorporate simultaneously with external fields while observing the real-time evolution of AFM domains.⁷⁵⁾ Another widespread technique involves scanning microscopies such as spin-polarized tunnelling microscopy⁸⁸⁾, magnetic exchange force microscopy⁸¹⁾, single spin scanning magnetometer⁸⁹⁾, and scanning thermal gradient microscopy⁹⁰⁾. These scanning

methods can deliver high-resolution AFM domain patterns, but they are still considered to be time-consuming and not easily accessible.⁷⁵⁾

From these viewpoints, microscopy utilizing the magneto-optical birefringence (MOB) effect serves as a practical, simpler, and more efficient tabletop technique that can visualize AFM domains in real-time under external fields, offering an advantage over other methods. The fundamental mechanism of MOB microscopy is based on the quadratic magneto-optical effect, where different spin orientations in AFM domains exhibit distinct anisotropies that affect the propagation of the incident light.⁷⁵⁾ This occurs because the magnetic ordering breaks the crystal's optical symmetry, leading to domain-dependent variations in the refractive indices. Accordingly, when the polarized light passes through regions with varying refractive indices, it acquires different phase retardations and polarization rotations, resulting in measurable birefringence in the form of high- and low-contrast regions.

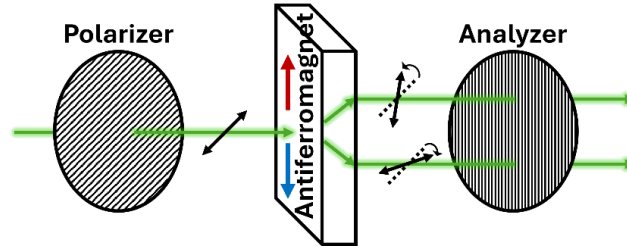


Figure 2.5. Magneto-optical linear birefringence of an antiferromagnet in transmission geometry

In the transmission geometry of MOB, the polarization of the light after transmission through the sample rotates by an angle θ and becomes partially elliptically polarized, with an ellipticity η .^{91),92)} This is a consequence of the varying refractive indices for light parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the magnetization M , and the birefringence that arises from this anisotropy⁹³⁾ can be expressed as

$$\Delta n = n_{\parallel} - n_{\perp} = K M^2 \quad \text{Eq. (2.5)}$$

K represents the Voigt constant (material-dependent quadratic magneto-optical coefficient). And the induced phase retardation between the two orthogonal polarization components is ⁹⁴⁾

$$\delta = \frac{2\pi d}{\lambda} \Delta n \quad \text{Eq. (2.6)}$$

where λ is the wavelength, and d is the optical path length (sample thickness).

For simplicity, if we suppose the linearly polarized light hits the surface of the magnetic material at normal incidence, with the magnetic moments oriented in-plane (Voigt rotation), the rotation angle would be ⁹³⁾

$$\theta = K \sin(2\phi) \quad \text{Eq. (2.7)}$$

ϕ is the angle between the electric vector E of the light and the magnetization M.

For the case with $\phi = 45^\circ$, the rotation and ellipticity will reach their peak, and maximum birefringence is achieved.

The MOB effect in transmission geometry is generally much weaker than linear magneto-optical effects and is therefore less frequently implemented to analyze magnetic materials.^{75),95)–99)} However, for our material of interest, bulk NiO, the MOB effect was discovered to be quite strong; therefore, transmission optical microscopy can be effectively implemented.¹⁰⁰⁾

2.3. Phonon-mediated exchange interactions

Many material properties are influenced by interactions among quasiparticles. Specifically, phonons' interactions with other quasiparticles play a key role in influencing material properties. For instance, anharmonic phonon-phonon interactions determine thermal conductivity and enable phenomena such as negative thermal expansion or ultralow thermal conductivity.¹⁰¹⁾ Electron-phonon interactions determine the temperature dependence of electrical resistivity in metals, carrier mobility in semiconductors, optical absorption in indirect-gap semiconductors, and the Cooper-pairing mechanisms of conventional superconductors.^{102),103)} Spin-phonon interactions are fundamental to phenomena such as magnetoresistance, magnetothermal transport, multiferroicity, magnetic phase transitions, and other magnetoelastic effects.^{104)–107)} In exotic systems, these can lead to emergent phenomena associated with quantum-mechanical many-body interactions.¹⁰⁸⁾ Especially in strongly correlated materials, phonons' degrees of freedom significantly feed back into the electronic and spin subsystems and can serve as tools to manipulate emergent phases.

2.3.1. Phonon-phonon interaction

Phonon-phonon interactions govern key material properties, including lattice thermal conductivity, infrared, Raman, neutron scattering cross sections, and phonon lifetimes.^{101),109)} In perfectly harmonic crystals, phonons are independent modes. Phonon-phonon interactions arise due to the anharmonicity of the interatomic bonds in crystals, deviating from the idealized harmonic oscillator model. Anharmonic interactions lead to the decay of phonons (e.g., three- and four-phonon processes), setting a limit on thermal transport and modifying equilibrium material properties, including thermodynamic stability, heat capacity, and other optical properties.^{101),109)} Without anharmonicity, phonons would have infinite lifetimes and would conduct heat without any resistance. The likelihood of specific phonon-phonon processes is

governed by selection rules based on energy and momentum conservation, as well as crystal symmetry.¹⁰⁹⁾

Phonon anharmonicity (phonon-phonon interaction) can be examined by techniques such as (1) inelastic neutron scattering^{62),63)} by measuring phonon dispersion relations and the lifetime of crystals under various environmental conditions, such as different temperatures, pressures, and external electric or magnetic fields, (2) inelastic X-ray scattering^{110),112)} to measure the energy exchange between the X-ray and the lattice, (3) X-ray diffuse scattering surpasses the above techniques by providing the ability to resolve individual decay channels of a specific phonon mode, offering a unique perspective on the phonon-phonon scattering process¹¹³⁾, and (4) ultrafast double pump-probe spectroscopy^{114),115)} to directly observe the frequency shifts of Raman phonons as a function of the oscillation amplitude and disentangle the coherent contribution from quasi-harmonic sources such as temperature and changes to the carrier density.

2.3.2. Electron-phonon interaction

As electrons travel through a crystal lattice, their movement can influence lattice vibrations, altering their energy and momentum. Electron-phonon interactions form the foundation of condensed matter physics, fundamentally influencing several phenomena. Lattice distortions and vibrations interact with electronic structures, affecting carrier mobility. Conversely, electron-phonon coupling can limit carrier mobility, which is a primary factor for thermal conductivity, by scattering phonons. This interaction is also responsible for conventional superconductivity. Phonon exchange effectively mediates an attraction between two electrons within a certain energy range, leading to the formation of a Cooper pair. The interplay between phonon-mediated attraction and electron-electron repulsion determines the superconducting transition temperature and influences the critical properties of superconductors. When electron-

phonon coupling is strong, an electron can deform the surrounding lattice, followed by the creation of a hybrid quasiparticle consisting of an electron dressed by a cloud of phonons called a polaron. Polarons have a larger effective mass than a free electron, and substantially mediate the system's mobility and optical absorption.^{116),117)} Electron-phonon interactions are also found to be one of the dominant contributors to the phonon lifetimes, particularly at low to moderate temperatures.¹¹⁸⁾

2.3.3. Spin-phonon interaction

When lattice vibrations alter the distances between magnetic ions or their local environment, the energies and orientations of spins can be affected. Conversely, these switching or relaxing spins can transfer energy back to the lattice in the form of phonons. This interaction between electronic spins and lattice vibrations is the core mechanism driving spin relaxation, magnetoelastic effects, magnetic transport, and phase transitions in magnetic materials. The pre-existing exchange interaction in the materials underlines the ground-state magnetic order, while the spin-phonon interaction enables the mutual coupling and transfer of spin angular momentum between the magnetic and lattice degrees of freedom.⁸⁾ The strength of spins' exchange interactions, which is responsible for different magnetisms, depends on interatomic distances. Phonons module these distances and dynamically alter the magnetic ordering of materials. Thus, this coupling forms a core foundation in the fields of spintronics and quantum information technologies. The spin lifetime in insulating materials is essentially limited by the spin-phonon coupling. At finite temperatures, spins can absorb or emit one or multiple phonons from or into the lattice and relax to an equilibrium state.¹¹⁹⁾ This is described by mechanisms such as Orbach, Raman, and direct spin-lattice relaxation processes, which are further explained in Section 2.4.2. And, since phonons are heat carriers, coupling to spins provides extra channels for heat dissipation and conversion between magnetic and thermal energy. In magnetic insulators, spin-phonon coupling plays a crucial role in understanding thermal

conductivity. However, many aspects of the interaction between phonons and spin degrees of freedom, such as the selection rules for spin-phonon interactions, the underlying mechanism of spin dissipation through lattices, and the quantification of spin-phonon coupling strengths, remain unclear.¹²⁰⁾

2.3.4. Magnon-phonon interaction

Magnon-phonon interactions arise from the coupling between spin waves (magnons) and phonons in magnetic materials. The core mechanisms behind this coupling involve magnetoelastic interaction and spin-phonon coupling. The strength of magnon-phonon coupling is fundamentally connected to the magnetostriction coefficient of the material, which quantifies how magnetic moments couple to lattice deformations. When phonons and magnon modes approach resonance, they undergo strong interaction characterized by an avoided crossing in the dispersion relation where the degeneracy is lifted and a hybridization gap opens.^{121)–125)} Strong magnon-phonon couplings create hybrid quasiparticles called magnon polarons, whose properties are distinct from pure magnons.^{121)–125)} They modify the dispersion of both magnons and phonons, affecting the thermodynamics and transport properties of the materials. Magnon polarons are also found to exhibit exceptionally long lifetimes resulting from hybridization with long-lived phonons.¹²⁴⁾

2.4. Phonon-assisted processes

Phonon-assisted processes stem from the aforementioned quantum mechanical interactions among quasiparticles and are crucial for understanding the optical properties, electronic transport, magnetization dynamics, and spin relaxation in all ranges of materials. For phonon-assisted processes to be accomplished, the symmetry of the phonon mode, exciton state, and photon polarization must follow specific selection rules that dictate which transitions are

allowed.^{126)–128)} However, high resonance, strong coupling, or defect-assisted processes can relax or break these rules, enabling new or otherwise forbidden transitions.^{127),129)}

2.4.1. Phonon-assisted electronic transition

Phonon-assisted electronic transition refers to processes where electrons in a material transit from one energy level to the other with the help of phonons. Therefore, instead of a direct transition, this process involves the absorption or emission of phonons to fulfil energy and momentum conservation throughout. This mechanism is important when direct electronic transitions are forbidden or inefficient, as phonons are necessary to enable or enhance these transitions. For instance, as in semiconductors with indirect band gaps, phonon-induced electronic transition must be accompanied by phonon absorption or emission. The earliest recognition of this mechanism came from optical studies of silicon and germanium, where indirect inter-band absorption was found to require the simultaneous absorption or emission of a phonon to overcome the momentum mismatch between the valence and conduction bands extrema.¹³⁰⁾

Phonon-assisted electron transition thus satisfies

$$E_{final} - E_{initial} = \hbar\omega_{photon} \pm \hbar\omega_{phonon} \quad \text{Eq. (2.8)}$$

, where the sign $\pm$ indicates whether a phonon is emitted (-) or absorbed (+).

$$\text{and } \vec{k}_{final} - \vec{k}_{initial} = \vec{q}_{photon} + \vec{q}_{phonon} \quad \text{Eq. (2.9)}$$

, where the phonon vector $\vec{q}_{phonon}$ is typically much larger than the photon wavevector in visible or infrared spectroscopy because phonon frequencies are much lower than electronic transition frequencies. $\vec{q}_{photon} \sim 0$ and $\vec{q}_{phonon}$ provides the needed momentum transfer. A study by Patrick et al.¹¹⁷⁾ developed a comprehensive theoretical framework explaining how phonons facilitate optical absorption, enabling electron transitions across energy levels that would

otherwise be forbidden, particularly in indirect-band-gap materials. Many experimental studies later provide strong evidence for this phenomenon.^{131),132)}

Anti-Stokes photoluminescence represents an important phonon-assisted process where an electron absorbs a photon with energy lower than the band gap by simultaneously absorbing phonons from the lattice. The electron is then excited to an electronic state by absorbing both a low-energy photon together with one or more phonons. Following thermalization in the excited state, the electron recombines by emitting a photon with higher energy. This process depends on the thermal population of phonons. In nanostructured materials, the probability of phonon-assisted anti-Stokes excitation can be significantly enhanced due to stronger electron-phonon coupling in the reduced-dimensional systems.¹³³⁾

2.4.2. Phonon-assisted spin alignment

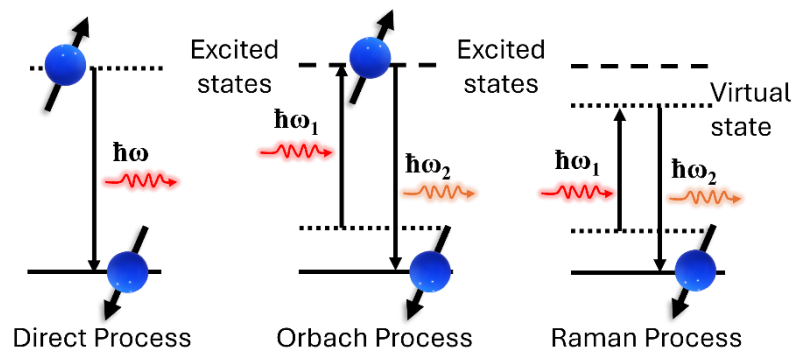


Figure 2.6. Spin-lattice relaxation in direct, Orbach, and Raman processes

Phonon-assisted spin alignment also follows a similar phenomenon. It refers to the processes when phonons mediate transitions between different spin states or facilitate spin reorientations through the transfer of angular momentum and quantum mechanical interactions. This is particularly significant in systems where external magnetic interactions or electromagnetic radiation cannot directly or efficiently drive spin transitions. Therefore, phonon-assisted spin alignments provide microscopic pathways for controlling spins via vibrational excitations.

As the phonons drive the spin-state changes, they impact the magnetization and spin relaxation dynamics. Spin-lattice relaxation time (denoted by T_1) arises from several different phonon-mediated processes, and ranges from nanoseconds to hundreds of seconds depending on the temperature and specific systems.¹³⁴⁾

(1) Direct process (one-phonon assisted relaxation)

Spin-lattice relaxation via direct process is a fundamental one-phonon-assisted transition which occurs by absorbing or emitting a single phonon whose energy matches the Zeeman splitting (energy difference between spin states when placed in an external magnetic field).¹¹⁹⁾ The direct process is dominant at low temperatures and high magnetic fields.^{135),136)} The spin-lattice relaxation time $T_{1, \text{Direct}}$ shows linear dependence on the temperature and external magnetic field.

$$T_{1, \text{Direct}} = C \frac{1}{B^m \coth(\frac{\Delta E}{2k_B T})} \quad \text{Eq. (2.10)}$$

($\Delta E = g\mu_B B$, Zeeman splitting energy)

$$T_{1, \text{Direct}} = C \frac{1}{B^m \coth(\frac{g\mu_B B}{2k_B T})} \quad \text{Eq. (2.11)}$$

And using, $\coth x = 1 + \frac{2}{e^{2x} - 1}$

$$T_{1, \text{Direct}} = C \frac{1}{B^m [1 + \frac{2}{(\exp(\frac{g\mu_B B}{k_B T}) - 1)}]} \quad \text{Eq. (2.12)}$$

where g is the Landé g -factor, μ_B is the Bohr magneton, and B is the magnitude of external magnetic field. C represents the material-dependent spin-phonon coupling constant and exponent depending on the type of spin system.

(2) Orbach process (two-phonon assisted spin relaxation)¹³⁵⁾

This involves the absorption or emission of a single phonon whose energy matches the spin transition through real intermediate electronic or spin states, followed by the emission or absorption of a phonon to relax back to the ground state. The spin-lattice relaxation rate (inverse of T_1) depends on the phonon energy resonance, as the relaxation is most efficient when available phonon frequencies match the transition energies. The Orbach process dominates at higher temperatures, where excited states can be easily accessible via thermal phonons.^{134),136)}

In this process, $T_{1, \text{Orbach}}$ is denoted as

$$T_{1, \text{Orbach}} = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad \text{Eq. (2.13)}$$

where τ_0 represents the material-dependent pre-exponential spin-phonon coupling constant, ΔE represents the energy difference between the transition levels, k_B is the Boltzmann constant, and T is the temperature.

(3) Raman process (two-phonon assisted relaxation)

The Raman spin relaxation process involves two-phonon interactions, where transitions occur through simultaneous absorption or emission of phonons. Unlike the Orbach process, these transition states are virtual. The Raman process is dominant at low to intermediate temperatures, where the Orbach process is suppressed.¹³⁷⁾ The spin-lattice relaxation time $T_{1, \text{Raman}}$ for this process can be denoted as

$$T_{1, \text{Raman}} = A \frac{1}{T^n} \quad \text{Eq. (2.14)}$$

where A represents the material-dependent spin-phonon coupling constant, and n is the temperature exponent depending on the type of spin system and phonon scattering mechanism (typically ranging from 3 to 9).¹³⁶⁾

Chapter 3

Experimental configuration

3.1. Selective phonon excitation via a mid-infrared laser

Direct irradiation of target phonon modes is one of the most effective and straightforward methods currently available. This approach depends on the direct interaction between electromagnetic waves and the dipole created by two atoms. Only optical phonon excitation is feasible here because acoustic phonon modes do not induce a change in the dipole moment. Many optical phonon frequencies of wide bandgap materials fall under the mid-infrared region^{138)–142)} and are therefore directly accessible with mid-infrared laser irradiations. Resonant excitations ensure minimal coupling to unwanted modes, making them ideal for cases that require precise control and minimal interference. Additionally, it typically requires low fluences compared to non-resonant methods, as the energy is directly coupled to the target phonon mode. This direct excitation method requires precise matching of the laser wavelength with the phonon absorption wavelength to ensure only the targeted optical phonon mode is excited. Furthermore, to avoid thermal excitation of the phonons caused by laser irradiation, the pump laser pulse width must be shorter than the phonon decay time.

3.1.1. Mid-infrared free-electron laser (MIR-FEL)

Among light sources capable of such phonon excitations, free-electron lasers offer unique advantages due to their high intensity, tunability, and narrow bandwidth characteristics. The mid-infrared free-electron laser (MIR-FEL) established at the Kyoto University Free Electron Laser (KU-FEL) facility, Institute of Advanced Energy (Kyoto University), is a suitable light

source to study selective phonon excitation. The characteristics of MIR-FEL, which is applied as the pump laser source for phonon excitations, are further described in detail.

The KU-FEL facility currently provides two electron accelerator-based light sources: a short-pulsed mid-infrared free electron laser (MIR-FEL) and a terahertz coherent undulator radiation source (THz-CUR). MIR-FEL consists of a 4.5-cavity RF electron gun and an energy filtering dog-leg section, a constant gradient type 3-meter-long accelerator tube, an 180° arc bunch compression section, a 1.8 m long hybrid undulator, a 5-meter optical resonator, and a beam dump section. A single-crystal Lanthanum hexaboride (LaB₆) thermal cathode of 2 mm in diameter is employed in the RF electron gun for both thermionic emission and photocathode operation. This thermionic RF gun generates an 8.3 MeV macro-pulse electron beam, which is then accelerated up to a maximum of 40 MeV in the accelerator tube. Both RF guns and accelerator tubes are driven by microwave amplifiers (Klystrons) operating at 2856 MHz (S-band) microwave frequencies. These accelerated high-energy beams are then injected into the hybrid undulator after being bunch-compressed by dipole and quadrupole magnets along the way. The undulator is where spontaneous radiation is emitted and amplified hundreds of times continuously by the injected electron beams before power saturation is achieved. A schematic diagram of the MIR-FEL configuration in the KU-FEL facility is shown in the Figure 3.1 (left).

The pulse structure of MIR-FEL is composed of two types, macro pulses and micro pulses (shown in Figure 3.1. (right)). The duration of the macro pulses and micro pulses are measured to be 2 μ s (FWHM) and 0.6 ps (FWHM) at 12 μ m.¹⁴³⁾ The macro pulse repetition frequency is at 2 Hz, and the micro pulse is 2856 MHz, and therefore contains an estimated 6,000 micro-pulses in each macro-pulse cycle.¹⁴³⁾ Presently, MIR-FEL can provide high-intense ultrashort mid-infrared pulses and can access vibrational excitations within the range of 3.4 to 26 μ m.¹⁴³⁾

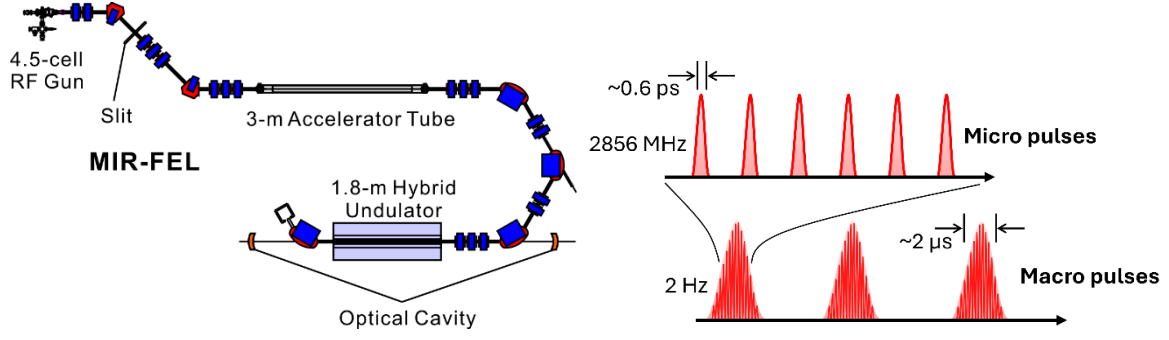


Figure 3.1. (left) Schematic diagram of MIR-FEL from the KU-FEL facility¹⁴³⁾, (right) macro and micro pulse structures of MIR-FEL from the KU-FEL facility

If the target phonon mode is infrared-active, it can be directly excited by tuning the MIR-FEL to match its energy. This is a one-photon (linear) absorption process, following standard selection rules. Such excitation has been demonstrated for the FLO(0) mode in 6H-SiC, A_1 (LO) mode in GaN, and B_u (LO) mode in DyFeO_3 .^{13),141),144)} However, if the desired phonon is infrared-inactive, a two-photon (non-linear) optical process is required for the excitation to be accomplished. In this process, the MIR-FEL is tuned so that its photon energy is half that of the target phonon mode. This allows the two photons to be absorbed simultaneously, enabling the excitation of modes that are forbidden in the linear process. This has also been experimentally demonstrated for the T_{2g} mode in diamond.^{145),146)}

3.1.2. Pump-probe measurement

After determining how the phonons will be pumped, it is next to consider how the pump modes will be observed and verified. Optical phonon modes can be directly excited by infrared absorption, in which the IR photon energy is converted into lattice vibrational energy without involving electronic excitation that would require higher-energy photons. In cases where vibrational assistance is absent, the emitted radiation will have the same frequency as the incident radiation, known as Rayleigh scattering. Conversely, when phonon-assisted processes occur, the emitted radiation will have a different frequency due to infrared absorption. This is

referred to as Raman scattering. Stokes Raman scattering provides information about ground-state phonons, while information about excited phonon states can be obtained from anti-Stokes Raman scattering. The intensity of the anti-Stokes scattered light depends on the population in the vibrationally excited state. Generally, the anti-Stokes scatterings have relatively weaker intensities unless the excited-state population is significantly higher. (More details on Raman scattering spectroscopy are provided in Chapter 2, section 2.1.2.1)

In the KU-FEL facility, in addition to the MIR-FEL, other light sources such as nanosecond (ns-Nd:YAG) and picosecond (ps-Nd:YVO₄) lasers are also available. By implementing MIR-FEL as a phonon pump source and an additional laser as a light source for anti-Stokes Raman scattering, a technique usually known as the pump-probe measurement. This technique enables real-time monitoring of phonon dynamics and can offer insights into both excitation mechanisms and subsequent relaxation processes. The process is that the selectively excited phonon via MIR-FEL irradiation will assist electrons transitioning from the ground state to an excited state. The excited electrons will then generate anti-Stokes scattering that contains information about the selectively excited phonon mode. However, this needs to be performed at an adequately low temperature, where all thermal excitations are suppressed and the electron population in the vibrationally excited state is negligible. A schematic diagram illustrating the pump-probe measurement mechanism of anti-Stokes Raman scattering resulting from MIR-FEL-induced phonon excitation is presented in Figure 3.2.

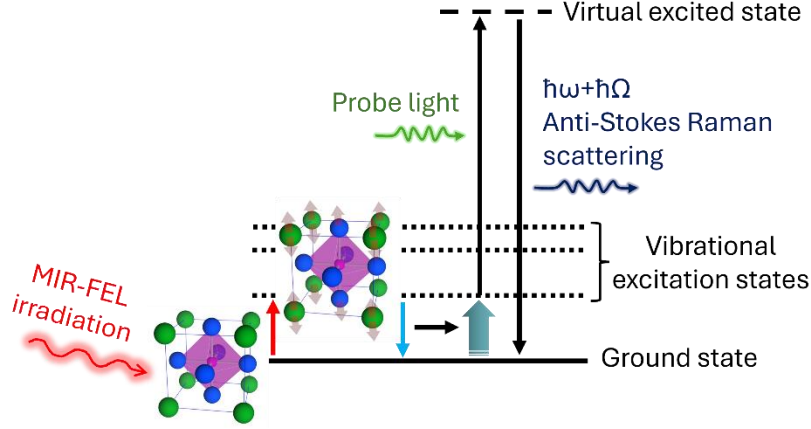


Figure 3.2. Anti-Stokes Raman scattering from MIR-FEL induced selective phonon excitation

3.2. Timing synchronization

For such pump-probe experiments, especially when aiming for nonlinear responses from the materials, precise control of both spatial and temporal overlap is essential. If the lasers to be implemented have different pulse durations and repetition rates, synchronization adjustment becomes inevitable, especially for this experimental observation of selectively excited phonons. While it is possible to easily align the spatial overlap of the two laser beams on the sample surface, temporal synchronization must be performed through a sequence of controlled steps. A straightforward method to verify the adjustment and optimal overlapping condition is through Sum Frequency Generation (SFG). This method relies on identifying the highest-intensity SFG signal via relative timing, thereby confirming that the two lasers are synchronized.

This timing synchronization via SFG observation can be performed on all nonlinear surfaces and interfaces where the inversion symmetry is broken. For this observation, we used commercially available Zinc Sulfide (ZnS Cleartran®) (ZnS Cleartran; ZSC25-2, Pier Optics Co., Ltd) of 12.5 mm in diameter and 2 mm thickness. ZnS Cleartran® has already been verified to be a nonlinear optical material in previous studies.^{145),146)} MIR-FEL of pulse

wavelength 12.5 μm (macro pulse intensity of 8 mJ, with each micro-pulse reaching 1.3 μJ) and a ps-laser (Nd: YVO₄) of wavelength 1064 nm (pulse intensity of 450 μJ) was implemented for this SFG observation. Accordingly, a conventional SFG spectrum is expected to occur at 980 nm.

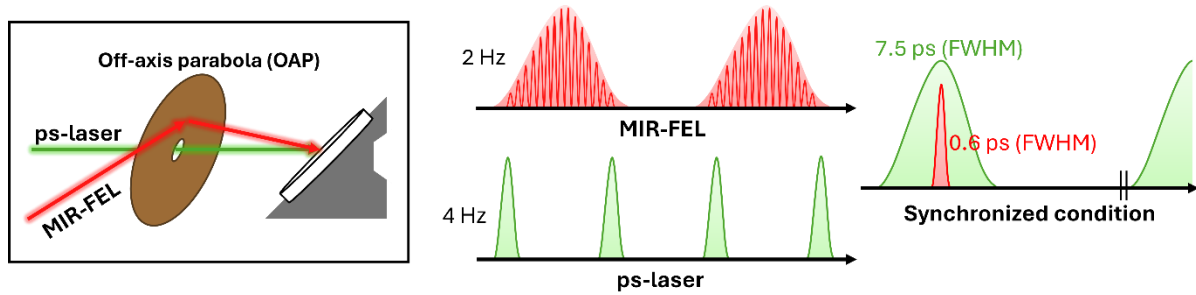


Figure 3.3. Spatial overlapping and timing synchronization of MIR-FEL and ps-laser

The relative timing of the ps-laser and MIR-FEL pulses was controlled using an electrical trigger signal. The length of the ps-laser cavity was adjusted to match the repetition rate of the ps-laser pulses with the reference RF signal used for electron beam acceleration in the MIR-FEL. An optical delay stage in the ps-laser path allowed precise control of the timing between the two pulses. An off-axis parabola (OAP) with a hole in the middle was positioned to focus the MIR-FEL on the sample surface, while the ps-laser beam passed through the hole in the OAP to reach the sample. Spatial overlap of the ps-laser and MIR-FEL beams on the sample was achieved by adjusting the OAP's tilt angle. Backscattered light from the crystal sample was collected using a collimator lens with a 50 mm focal length. A 700 nm long-pass filter was placed in the path of the scattered beam. Additionally, notch filters at 532 nm (StopLine 532 Semrock) and 1064 nm (Thorlabs NF 1064-44) were used to remove strong scattered light before entering the spectrometer (Triax 190; Horiba Scientific). The incoming SFG light was then detected using an ICCD (image intensified charge-coupled device) camera (PI-MAX2; Princeton Instruments) connected to the spectrometer. A photomultiplier tube (PMT) (R3896, Hamamatsu Photonics), also attached to the spectrometer, was occasionally used to check the

delay time between the lasers with a digital oscilloscope (DPO 3054, Tektronix). This experiment was conducted at room temperature, and SFG spectra were recorded simultaneously with MIR-FEL on and off conditions by setting the ps-laser repetition rate to be twice that of the MIR-FEL macro pulses, at 4 Hz and 2 Hz, respectively.

3.2.1. Observation of high-order sum frequency generations

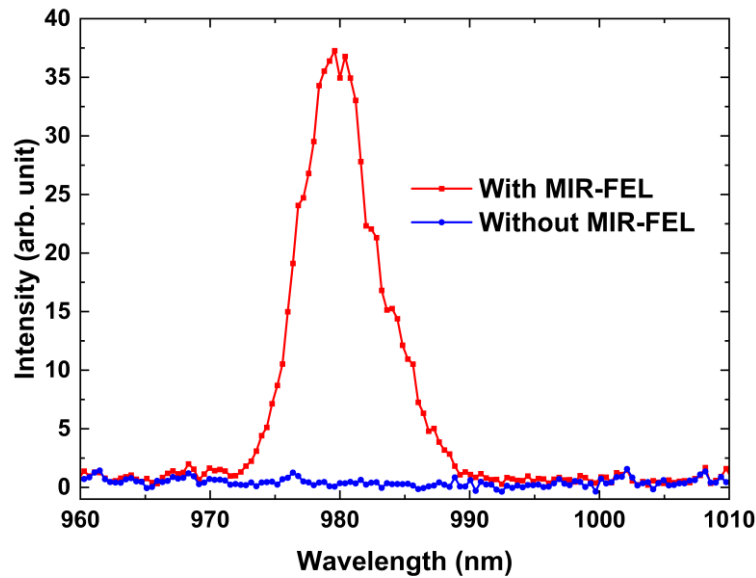


Figure 3.4. SFG from ZnS Cleartran® at 980 nm

Unforeseen spectra were also observed at around 910 nm and 848 nm, alongside the conventional SFG peak at 980 nm. (Figure 3.4) To verify these additional scattered wavelengths, a short-pass filter with a cutoff at 700 nm was replaced with a long-pass filter, and we found that all the peaks vanished. They only reappeared when the long-pass filter was reinserted. This confirmed that the observed peaks are from the scattered wavelengths longer than 700 nm.

Multi-photon injection from MIR-FEL is not a new occurrence, as previous studies have already implemented it to induce two-photon injections for the excitation of the infrared-inactive T_{2g} phonon mode in diamond.^{145),146)} Thus, it is convinced that more than one photon injection could be expected from our MIR-FEL beam as long as the pulse energy is sufficiently

high. That being said, the intensity of our observation (1.3 μJ) is comparatively high, even in relation to previous multi-photon studies, which employed 0.8 μJ ¹⁴⁵⁾ and 1.1 μJ ¹⁴⁶⁾. Accordingly, if we consider the process where two concurrent incoming photons from MIR-FEL overlap with a ps-laser pulse, the third-order SFG output (a three-photon process involving two MIR-FEL photons and one from the ps-laser) can be expected as

$$\lambda_{(2 \times \text{MIR-FEL} + 1 \times \text{ps-laser})} = \frac{1}{\frac{1}{12.5 \mu\text{m}} + \frac{1}{12.5 \mu\text{m}} + \frac{1}{1064 \text{ nm}}} = 909.21 \text{ nm}$$

Additionally, the peak at 847 nm is assumed to be the fourth-order SFG output (a four-photon process involving three MIR-FEL photons and one from the ps-laser).

$$\lambda_{(3 \times \text{MIR-FEL} + 1 \times \text{ps-laser})} = \frac{1}{\frac{1}{12.5 \mu\text{m}} + \frac{1}{12.5 \mu\text{m}} + \frac{1}{12.5 \mu\text{m}} + \frac{1}{1064 \text{ nm}}} = 847.56 \text{ nm}$$

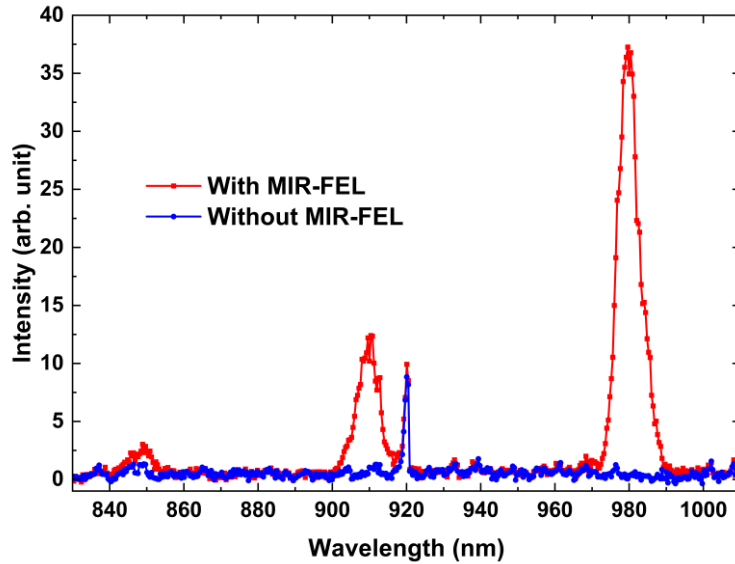


Figure 3.5. Sum Frequency Generations from ZnS Cleartran®

Furthermore, we could also observe an additional scattering spectrum at 510 nm. Respectively, if we stretch out this high-order SFG phenomenon, considering multiple photon injections from the ps-laser as well, the third-order SFG scattering (three-photon process of one photon from MIR-FEL and two from ps-laser) and a fourth-order SFG (four-photon process of two photons from MIR-FEL and two from ps-laser).

$$\lambda_{(1 \times \text{MIR-FEL} + 2 \times \text{ps-laser})} = \frac{1}{\frac{1}{12.5 \mu\text{m}} + \frac{1}{1064 \text{ nm}} + \frac{1}{1064 \text{ nm}}} = 510.28 \text{ nm}$$

The recorded MIR-FEL spectrum shape at 12.5 μm is shown in Figure 3.7. MIR-FEL spectrum at 12.5 μm . The MIR-FEL spectral line shape closely resembles the observed SFG spectra, especially in the conventional 980 nm and third-order SFG at 510 nm. This confirms that the spectra are indeed SFG outputs influenced by MIR-FEL. Additionally, based on previous findings of phonon dispersion and the density of states of ZnS Cleartran®¹⁴⁷⁾, we could recognize that there are no phonon absorption energies within our observation wavelength. Hence, it is also assured that vibrational Raman scattering did not contribute to this observation.

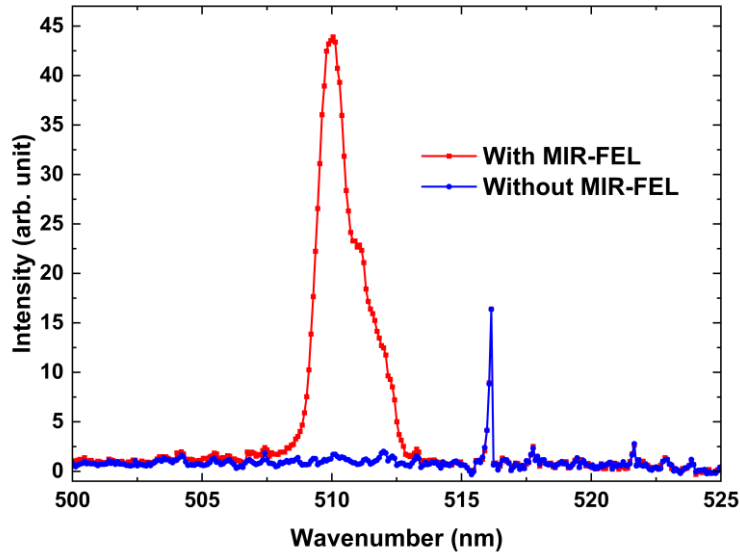


Figure 3.6. SFG from ZnS Cleartran® at 510 nm

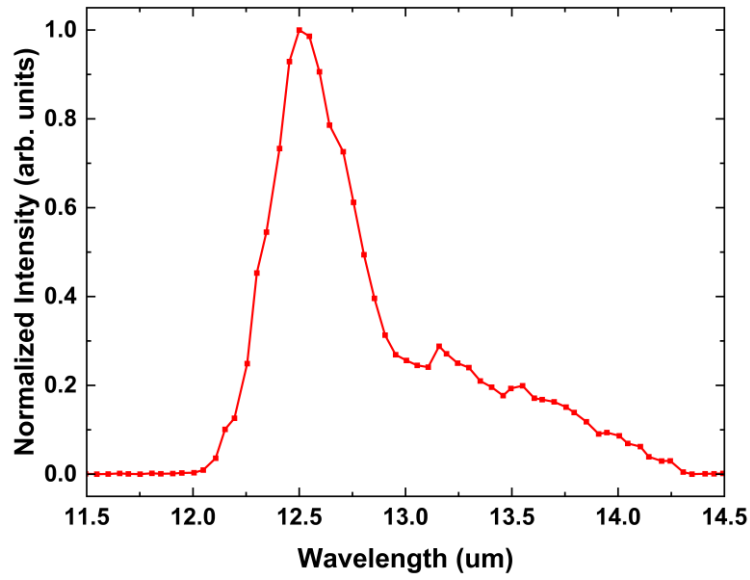


Figure 3.7. MIR-FEL spectrum at 12.5 μm

The synchronization condition of the two lasers can be determined by tracing the highest intensity SFG as the relative timing delay is adjusted. Figure 3.8. shows the SFG peak intensity at 510 nm against the delay time of the probe ps-laser to the pump laser (MIR-FEL). Accordingly, we were able to locate the optimal timing-synchronized condition of the pump and probe lasers.

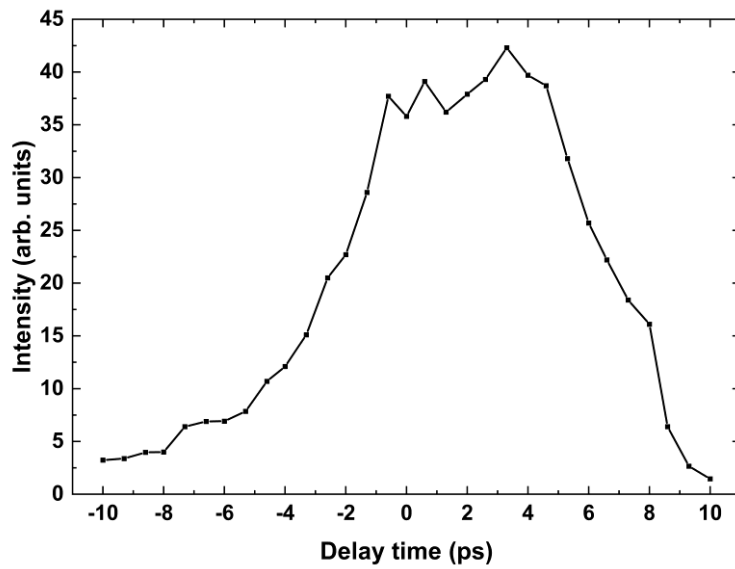


Figure 3.8. SFG intensity at 510 nm with respect to probe delay

Chapter 4

Selective Excitation of Raman Forbidden

Phonon Mode

4.1. Overview

Selective phonon excitations have been performed in several bulk wide-bandgap semiconductors via the pump-probe techniques using MIR-FEL from the KU-FEL facility as a pump source. The very first experiment was conducted by Yoshida et al., where they achieved the excitation of the FLO (0) mode (folded longitudinal optical mode at $x=0$) of 6H-SiC.¹⁴¹⁾ The phonon mode was both IR and Raman-active, and therefore, the confirmation of the selective excitation was done using anti-Stokes Raman scattering spectra with an ns-Nd:YAG laser probe. Applying the same method, Kagaya et al. also performed the excitation of the IR and Raman-active A_1 (LO) mode of GaN.¹⁴⁴⁾ For IR-inactive phonon modes, this single photon absorption of the phonon mode via the direct IR irradiation method is not accessible. Therefore, to achieve the selective excitation of an IR-inactive phonon, Oji Sato et al. and Akasegawa et al. implemented a two-photon irradiation method.^{145),146)} By tuning the MIR-FEL frequency to half the target phonon frequency, they bypassed the selection rule for IR-inactive modes and achieved excitation of the T_{2g} mode in diamond.

In these prior experiments, all observed phonon modes are Raman-active, and therefore these selective excitations can be confirmed by anti-Stokes Raman scattering. (More details are mentioned in Section 3.1.2, Chapter 3) However, for the phonon modes that are Raman forbidden, meaning they cannot be accessed with linear Raman spectroscopy due to symmetry selection rules, the above pump-probe technique will not be feasible. Accordingly, no Raman

inactive phonon modes have yet been experimentally proven to be selectively excitable using direct MIR-FEL irradiation. In order to bridge this observation gap, an alternative probing technique is required.

4.1.1. Hyper-Raman scattering spectroscopy

Here, we introduce one of the nonlinear Raman scattering processes, the hyper-Raman scattering (HRS). HRS is a second-order nonlinear optical process, which involves the interaction of light with vibrational modes through the hyperpolarizability tensor (β) (third-rank polarizability tensor), rather than the second-rank polarizability tensor (α) in linear Raman scattering. (More details in Section 2.1.2.1., Chapter 2) In this case, the induced second-order polarization (dipole moment), $P^{(2)}$ can be described as

$$P^{(2)} = \beta E_i^2 \quad \text{Eq. (4.1)}$$

And analogous to the Raman process, β can be described as

$$\beta = \beta_0 + \beta_1 \cos(2\pi\nu_p t) \quad \text{Eq. (4.2)}$$

And the incident light energy is $E_i = E_{i0} \hat{e} \cos(2\pi\nu_i t)$ as in eq (2.1),

Using $\cos^2(x) = \frac{1}{2}(1 + \cos 2x)$, and $\cos(x) \cos(y) = \frac{1}{2} \cos(x-y) + \frac{1}{2} \cos(x+y)$,

the $P^{(2)}$ can be derived as

$$\begin{aligned} P^{(2)} &= [\beta_0 + \beta_1 \cos(2\pi\nu_p t)] E_{i0}^2 (\hat{e}\hat{e}) \cos^2(2\pi\nu_i t) \\ &= E_{i0}^2 (\hat{e}\hat{e}) [\beta_0 \cos^2(2\pi\nu_i t) + \beta_1 \cos(2\pi\nu_p t) \cos^2(2\pi\nu_i t)] \\ &= E_{i0}^2 (\hat{e}\hat{e}) \left[\frac{1}{2} \beta_0 (1 + \cos(4\pi\nu_i t)) + \frac{1}{2} \beta_1 [\cos(2\pi\nu_p t) + \cos(4\pi\nu_i t) \cos(2\pi\nu_p t)] \right] \\ &= E_{i0}^2 (\hat{e}\hat{e}) \left[\frac{1}{2} \beta_0 + \frac{1}{2} \beta_0 \cos(4\pi\nu_i t) + \frac{1}{2} \beta_1 [\cos(2\pi\nu_p t) + \frac{1}{2} \cos(4\pi\nu_i t - 2\pi\nu_p t)] \right] \end{aligned}$$

$$+\frac{1}{2} \cos (4\pi\nu_i t + 2\pi\nu_p t)]$$

$$P^{(2)} = E_{i0}^2 (\hat{e}\hat{e}) \left[\frac{1}{2} \beta_0 + \frac{1}{2} \beta_0 \cos (4\pi\nu_i t) + \frac{1}{2} \beta_1 \cos (2\pi\nu_p t) + \frac{1}{4} \beta_1 \cos (2\pi (2\nu_i - \nu_p)t) \right.$$

$$\left. + \frac{1}{4} \beta_1 \cos (2\pi (2\nu_i + \nu_p)t) \right] \quad \text{Eq. (4.3)}$$

The second term represents elastic hyper-Rayleigh scattering, and the third term represents vibrational-induced modulation independent of the optical field. The fourth and fifth terms represent inelastic Stokes and anti-Stokes hyper-Raman scattering components, respectively.

Therefore, the HRS process involves two incident photons of the same energy ($2\nu_i$), and one photon with twice the incident energy (ν_p) is emitted. The frequency of the HRS light can be simply described as $\nu_{\text{HRS}} = 2\nu_i \pm \nu_p$, where $\pm$ denotes Stokes and anti-Stokes scattering processes.

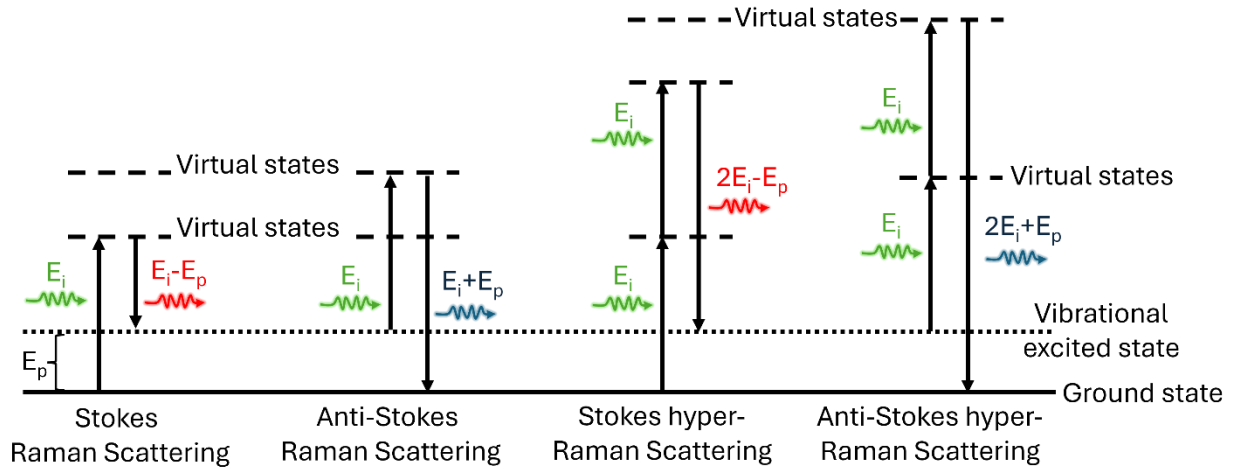


Figure 4.1. Comparison of Stokes and anti-Stokes Raman and hyper-Raman scattering processes

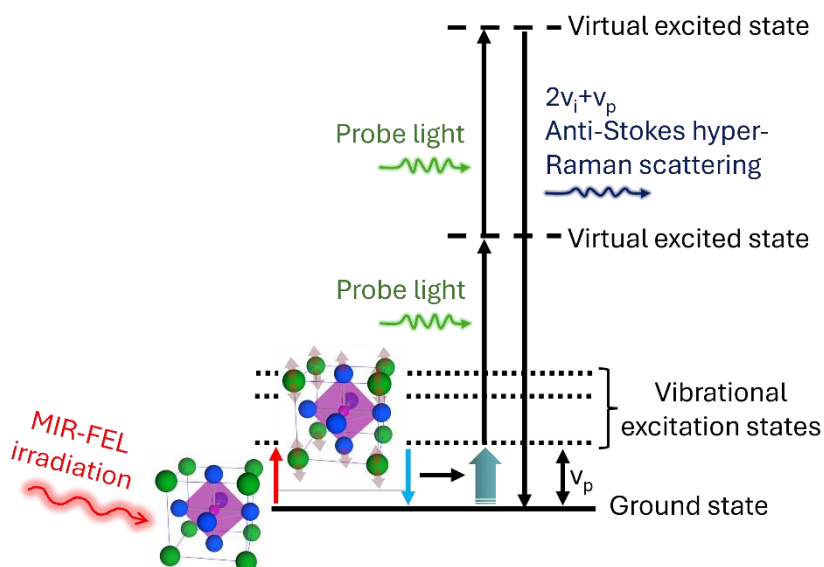


Figure 4.2. Anti-Stokes hyper-Raman scattering from MIR-FEL induced selective phonon excitation

HRS employs different selection rules, thereby making certain vibrations accessible that are forbidden in Raman and infrared spectroscopy. Some of the already proven and reported rules are that (1) IR active dipole vibrations are always HRS active despite the symmetry of the material, (2) rule of mutual exclusion occurs between Raman scattering and HRS spectra for centrosymmetric crystals, where only the even modes (gerade) are Raman active and only the odd modes (ungerade) are hyper-Raman active, and (3) the silent modes (both Raman and IR forbidden) may be active in HRS spectra.^{148),149)} Hyper-Raman scattering cross-section is typically several orders of magnitude weaker than that of conventional Raman scattering. And as being a spontaneous scattering process, the frequency resolution of the scattered signal depends on the frequency bandwidth of the excitation source. Therefore, high-power pulsed lasers are highly preferred for HRS experiments. Figure 4.2 shows the principle of how the MIR-FEL-induced selective phonon excitation will be observed via anti-Stokes HRS.

4.2. Crystal structure and optical phonon modes of SrTiO₃

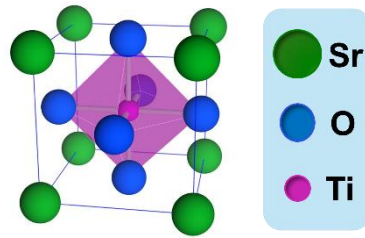


Figure 4.3. Crystal Structure of SrTiO₃

SrTiO₃ adopts a centrosymmetric cubic perovskite crystal structure, with the space group $Pm\bar{3}m$. The lattice structure of SrTiO₃ is composed of four TiO₆ octahedra surrounded by Sr²⁺ ions, resulting in a mixed ionic-covalent chemical bonding arrangement between them. The lattice parameter at room temperature is approximately 3.904 Å. The crystal structure can be oriented along common faces such as (100), (110), and (111), making it popular for epitaxial thin-film growth. Upon cooling, SrTiO₃ undergoes a structural phase transition from cubic to tetragonal, characterized by a space group of I4/mcm at the transition temperature $T_c = 105$ K.^{48),150)–153)} Then it transitions to orthorhombic around 65 K, and possibly to rhombohedral below 10 K.^{151),152)} Along with the tetragonal transition, the material approaches from its paraelectric phase to the ferroelectric phase, which instead undergoes a quantum paraelectric transition at 37 K due to quantum fluctuations.^{154),155)}

SrTiO₃ exhibits several unique properties that have led to extensive research and numerous discoveries in the past years. One of the several properties is that it exhibits a very high, tunable dielectric constant of 330 for the (100) plane orientation, 456 for the (110) plane, and 448 for the (111) plane at room temperature.³⁹⁾ The value increases to the order of 10⁴ in a very low external field and temperature, then stabilizes below 4 K.^{39),155)} The material also demonstrates outstanding photocatalytic activity and high specific capacitance, especially when synthesized with controlled morphologies that enhance surface area and defect density. This enhances its ability to split water under UV light and facilitates the photodegradation of dyes.^{156),157)}

Therefore, they are often as well researched as electrode materials in supercapacitors. SrTiO_3 can also be easily altered from insulating to semiconducting, metallic, and superconducting by doping, reducing oxygen content, and cooling.¹⁵⁸⁾ SrTiO_3 exhibits striking superconducting behavior with extremely low carrier concentrations, and the superconducting transition temperature (T_c) of SrTiO_3 highly depends on isotope concentration.⁴²⁾ Even though SrTiO_3 is the first perovskite oxide semiconductor discovered to exhibit superconducting behavior, the exact mechanism of this phenomenon remains unknown and remains an active area of research.

The material has recently attracted renewed attention due to the discovery of remarkable persistent photoconductivity. The electrical conductivity of SrTiO_3 increases by three orders of magnitude when illuminated with sub-gap light at room temperature and persists for weeks or longer without any noticeable decay.^{40),41)} This metastability is explained by a configuration in which the photoexcited electrons escape from deep defect levels and remain trapped in the conduction band until they overcome a substantial thermal recapture barrier. Such persistent photoconductivity behavior has been reported in other wide-bandgap semiconductors such as GaN and GaInNAs.^{159),160)} However, the magnitude of enhancement is much smaller than that in SrTiO_3 .

The phonon modes of single-crystal SrTiO_3 at the Γ -point in the Brillouin zone in the cubic phase can be assigned as $\Gamma = 4T_{1u} + T_{2u}$.^{48),148),161)} One T_{1u} mode is acoustic, and taking into account the TO-LO splitting¹⁶²⁾ of each T_{1u} polar mode, a total of seven optical phonon modes are observable in the SrTiO_3 . The optical T_{1u} modes (TO1, LO1, TO2, LO2, TO3, LO3) are infrared-active but Raman-inactive. The T_{2u} mode, which is only associated with the displacement of O atoms, is neither infrared nor Raman active and is therefore denoted as a silent mode. The T_{1u} modes are associated with polar displacements involving Ti-O stretching and bending vibrations. Among these, the LO3 mode corresponds to the high-frequency, collective out-of-plane dynamic displacements of oxygen atoms.⁴⁸⁾ Theoretically assigned

phonon modes locations using hybrid exchange-correlation functions are at 69 cm⁻¹, 175 cm⁻¹, 553 cm⁻¹, 180 cm⁻¹, 480 cm⁻¹, 809 cm⁻¹ for TO1, TO2, TO3, LO1, LO2, LO3, and 255 cm⁻¹ for T_{2u} mode, respectively.⁴⁸⁾

Table 4.1. Optical phonon modes of SrTiO₃ (NS represents neutron scattering spectroscopy, and IR represents infrared spectroscopy)

Modes		Theoretical Calculation ⁴⁸⁾	NS ¹⁵⁰⁾	IR ¹⁶³⁾	HRS ¹⁴⁸⁾	HRS (right-angle) ¹⁶⁴⁾	HRS (forward) ¹⁶⁴⁾
T _{1u}	TO1	84 cm ⁻¹	91 cm ⁻¹	88.5 cm ⁻¹	87 cm ⁻¹	84 ± 3 cm ⁻¹	79 ± 3 cm ⁻¹
	LO1	173 cm ⁻¹	175 cm ⁻¹	171 cm ⁻¹	179 cm ⁻¹	176 ± 5 cm ⁻¹	174 ± 3 cm ⁻¹
	TO2	176 cm ⁻¹	178 cm ⁻¹	174 cm ⁻¹			
	LO2	473 cm ⁻¹	476 cm ⁻¹	474 cm ⁻¹	472 cm ⁻¹	480 ± 5 cm ⁻¹	474 ± 3 cm ⁻¹
	TO3	544 cm ⁻¹	543 cm ⁻¹	543 cm ⁻¹	542 cm ⁻¹	544 ± 5 cm ⁻¹	552 ± 10 cm ⁻¹
	LO3	804 cm ⁻¹	825 cm ⁻¹	796 cm ⁻¹	792 cm ⁻¹	798 ± 5 cm ⁻¹	796 ± 3 cm ⁻¹
T _{2u} (soft mode)		255 cm ⁻¹	267 cm ⁻¹	-	265 cm ⁻¹	270 cm ⁻¹	264 cm ⁻¹

Since the first-order T_{1u} modes are Raman-forbidden in the cubic phase above 105 K, observing the phonon modes of SrTiO₃ requires specialized experimental approaches such as terahertz time-domain spectroscopy, coherent phonon spectroscopy, or hyper-Raman scattering spectroscopy. From the experimental observations, it has been discovered that the phonon modes of SrTiO₃ exhibit a remarkable temperature dependence, except for the LO3 mode.^{148),165)} The temperature dependency is most remarkable for the soft TO1 mode, whose frequency decreases from 90 cm⁻¹ at 300 K to 18 cm⁻¹ at 5 K.^{148),165)} The summarized comparison of the phonon mode frequencies at room temperature (~300 K) from theoretical

prediction and experimental values of neutron scattering, infrared spectroscopy, HRS in right-angle scattering geometry, and forward scattering geometry is presented in the Table 4.1.

4.3. Experimental Configuration

A SrTiO₃ single crystal substrate (Crystal Base Co., Ltd.) with a (111) plane orientation was used as our target sample. The crystal was grown using the Bernoulli method, resulting in a high-quality crystal with a purity of 99.99%. The substrate was polished on only one side for backscattering observation, as the rough, unpolished backside reduces unwanted reflections and interference, ensuring that the detected signals mainly originate from scattering within the bulk sample. The dimension of the substrate was 10 mm × 5 mm and 0.5 mm in thickness. The sample was placed on an aluminum sample holder within the vacuum chamber, equipped with specific optical windows. As shown in Figure 4.4, the KBr window was set to pass both the MIR-FEL beam and the probe light on the sample surface, while the CaF₂ window was placed for transmitted and scattered light. The cooling down was conducted using a cryostat (SRDK-205, Sumitomo Heavy Industries, Ltd.) equipped with a helium compressor (CKW-21, Sumitomo Heavy Industries, Ltd.).

Micro pulses of MIR-FEL, with 0.5 ps (FWHM) pulse duration and 2856 Hz repetition rate, and a picosecond laser (ps-Nd:YVO₄ mode-lock laser, Time-Bandwidth GE 100-VAN) with 7.5 ps (FWHM) pulse duration and 4 Hz repetition rate were employed as pump and probe light sources in this observation. The wavelength of the ps-laser is 1064 nm, and that of MIR-FEL was tuned at 12.5 μm to match the LO₃ phonon mode frequency. An off-axis parabola (OAP) with a hole was positioned to focus the MIR-FEL beam onto the sample surface, while the probe laser passed through the hole of the OAP and was incident on the sample. Spatial overlap of the ps-laser and MIR-FEL beams was achieved by adjusting the OAP's tilt angle, and temporal overlap was controlled via electric trigger signals. An optical delay stage was

employed in the ps-laser path for further precise adjustments. Zero delay in the relative timing between pump and probe pulses was achieved through SFG observation using a ZnS Cleartran® substrate attached adjacent to SrTiO₃, as shown in Figure 4.4. (Detail on this timing synchronization measurement between MIR-FEL and the ps-lasers is mentioned in Section 3.2, Chapter 3) The scattered light was collected using a collimator lens with a 50 mm focal length, which then passed through a notch filter of 532 nm. This will eliminate the strong second-harmonic generation (SHG) that might also be emitted from the crystal sample. This filter insertion, however, will not affect the detection of hyper-Raman scattering intensity. The scattered light then entered the spectrometer (Triax 190, Horiba Scientific) through an ICCD camera (PI-MAX2; Princeton Instruments) for detection.

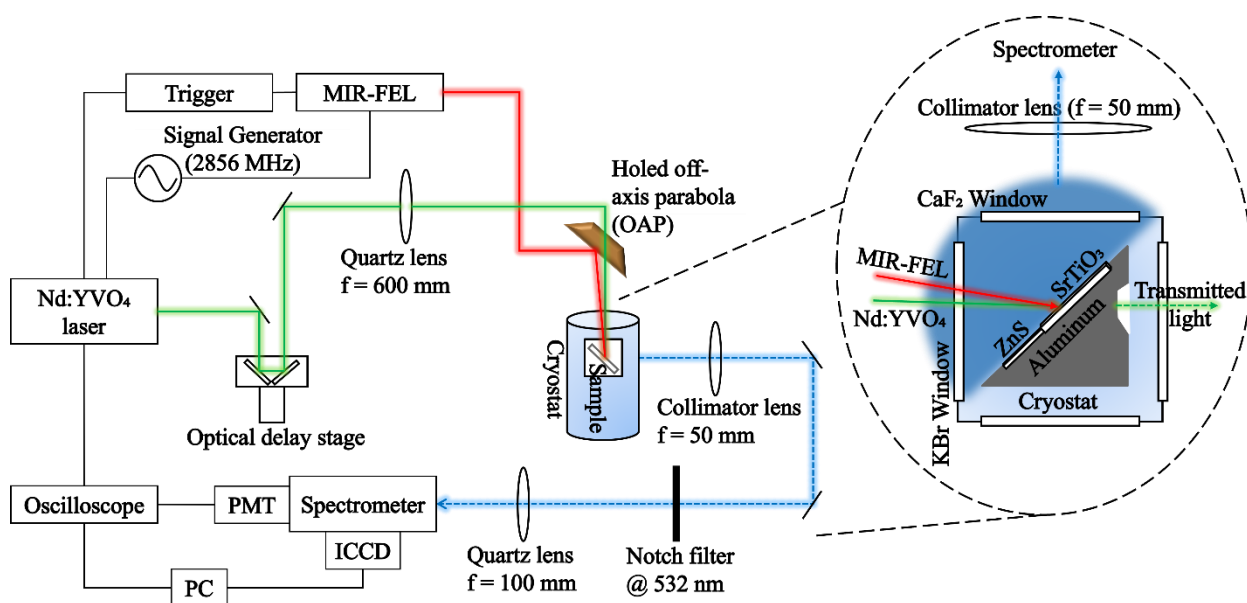


Figure 4.4. Schematic diagram of the experimental setup at cryogenic temperature¹³⁹⁾

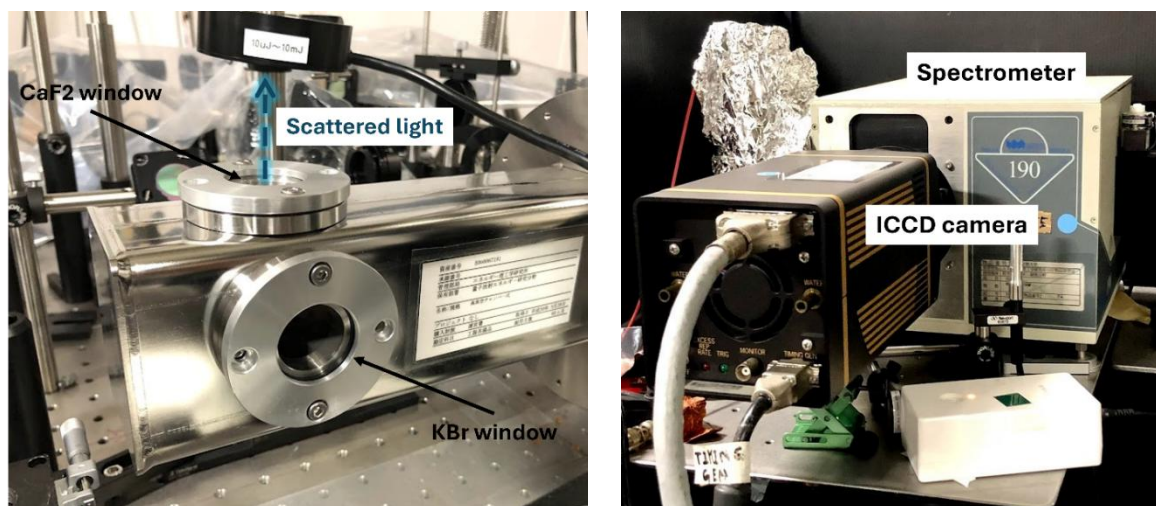


Figure 4.5. Photographs of the experimental setup, cryostat with specific optical windows during measurement (left), and detection setup with a spectrometer attached to the ICCD camera

4.4. Phonon modes confirmation from hyper-Raman scatterings

4.4.1. Room temperature measurements

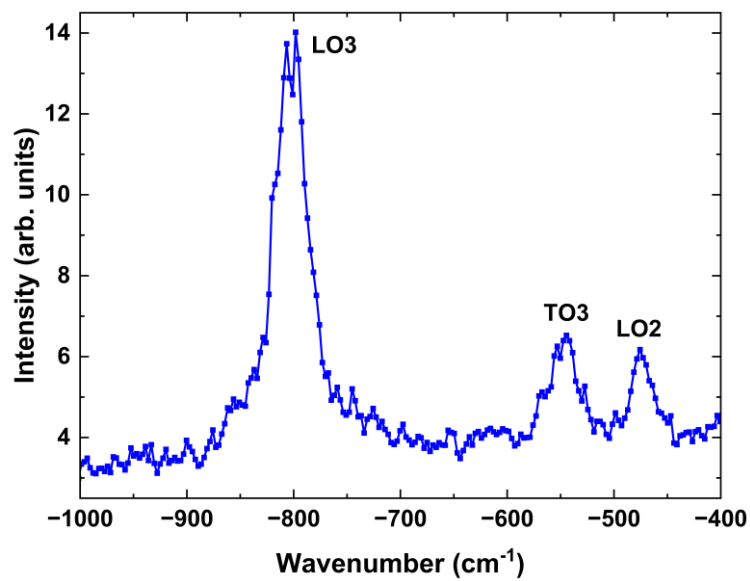


Figure 4.6. Stokes hyper-Raman scattering at room temperature, 0.1 mm spectrometer slit width (without MIR-FEL irradiation)

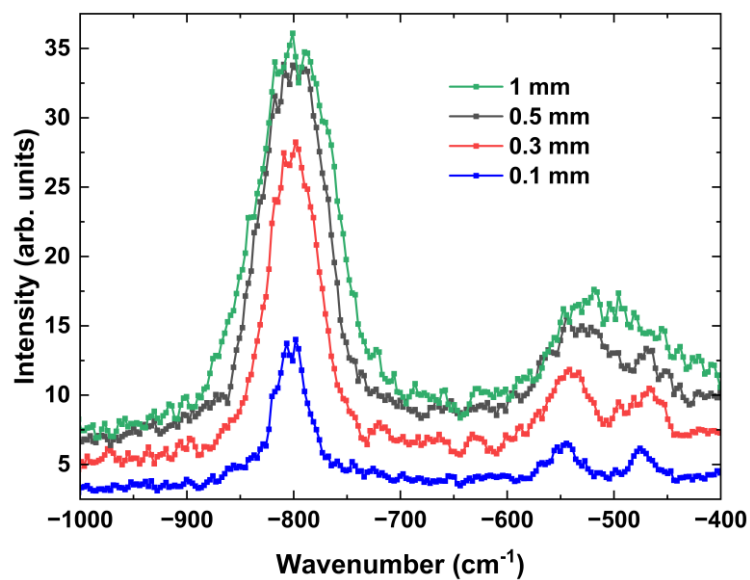


Figure 4.7. Stokes hyper-Raman scattering at room temperature with different spectrometer slit widths (without MIR-FEL irradiation)

First of all, the hyper-Raman scattering from the optical phonon modes of our SrTiO₃ sample without external excitation was confirmed at room temperature. The ps-laser energy was set around 1 mJ, and the spectrometer entrance slit width was 0.1 mm. We first recorded the Stokes hyper-Raman scattering. Three peaks at around -470 cm⁻¹, -540 cm⁻¹, and -800 cm⁻¹ have been detected, which can be assigned to the three phonon modes LO2, TO3, and LO3 among the total of seven. (The negative signs indicate Stokes scattering at lower energy levels compared to that of Rayleigh scattering, refer to Section 2.1.2.1. Chapter 2). The Figure 4.6 shows the recorded Stokes hyper-Raman scattering spectra measured with a spectrometer slit width of 0.1 mm at room temperature. As shown in the Figure, the LO3 phonon mode exhibits the highest Stokes HRS intensity among all observed modes. We then measure the Stokes hyper-Raman scattering intensity and the spectral resolution dependence on the spectrometer slit width by changing it from 0.1 mm to 0.3 mm, 0.5 mm, and 1 mm. The results can be seen in Figure 4.7. The significant increase in the LO3 phonon-scattering intensity at -800 cm⁻¹ is evident. While a slight separation of the LO2 (-470 cm⁻¹) and TO3 (-540 cm⁻¹) modes can still be observed with a 0.5 mm spectrometer slit, only a broad, mixed peak appears for these two modes at a 1 mm slit width. Based on this observation, we conclude that a spectrometer slit width of 0.3 mm is appropriate to produce enough intensity and resolution for recording the anti-Stokes HRS spectra.

We then continued measuring the anti-Stokes HRS using a 0.3 mm spectrometer slit at room temperature. Scattering spectra are expected to be much weaker intensity than those from the Stokes measurement. From the results shown in the figure, the Stokes scattering from the LO3 phonon mode remains clearly visible at 800 cm⁻¹, while broad and weak spectral peaks at ~545 cm⁻¹ and ~460 cm⁻¹ could possibly be attributed to scatterings from the TO3 and LO2 phonon modes.

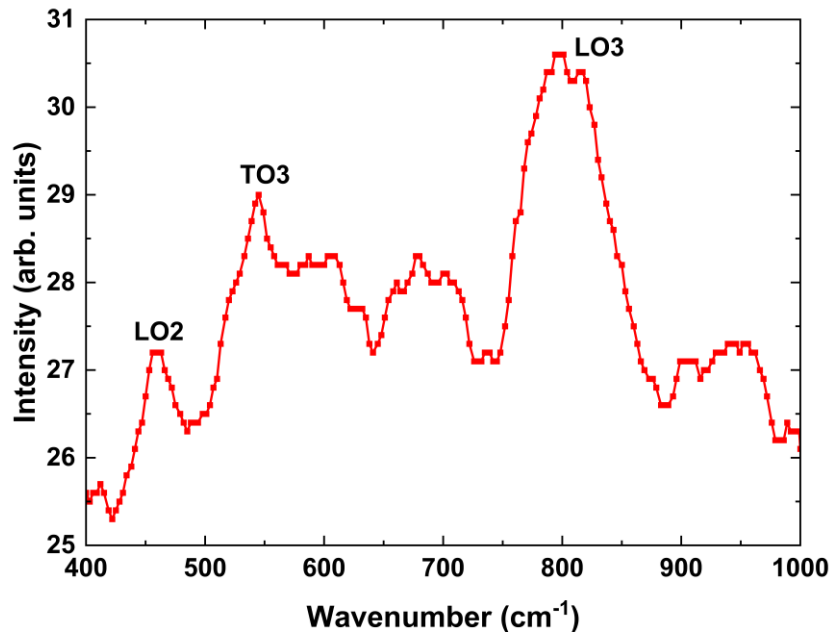


Figure 4.8. Anti-Stokes hyper-Raman scattering at room temperature with 0.3 mm slit widths
(without MIR-FEL irradiation)

4.4.2. Cryogenic temperature measurements

We further proceed with the observation at cryogenic temperature. The sample is placed inside the cryostat, as shown in the experimental setup (Figure), and cooled down to 5 K. This process eliminates all thermal excitations, leaving a negligible population in the excited states. The ps-laser intensity was set at ~ 1.8 mJ. We first recorded Stokes HRS. All three phonon modes LO2, TO3 and LO3 were observed at -470 cm^{-1} , -540 cm^{-1} , and -800 cm^{-1} , respectively. (Figure 4.9) We then recorded anti-Stokes HRS. As seen in Figure 4.10, all vibrational excitations were suppressed at this temperature, and no anti-Stokes scattering was observed. Figure 4.11 shows the comparison of the anti-Stokes hyper-Raman scattering at room temperature and at 5 K with different spectrometer slit widths. These comparison results confirm that no thermal excitations, especially at the LO3 phonon mode energy, are present at 5 K before irradiation with MIR-FEL.

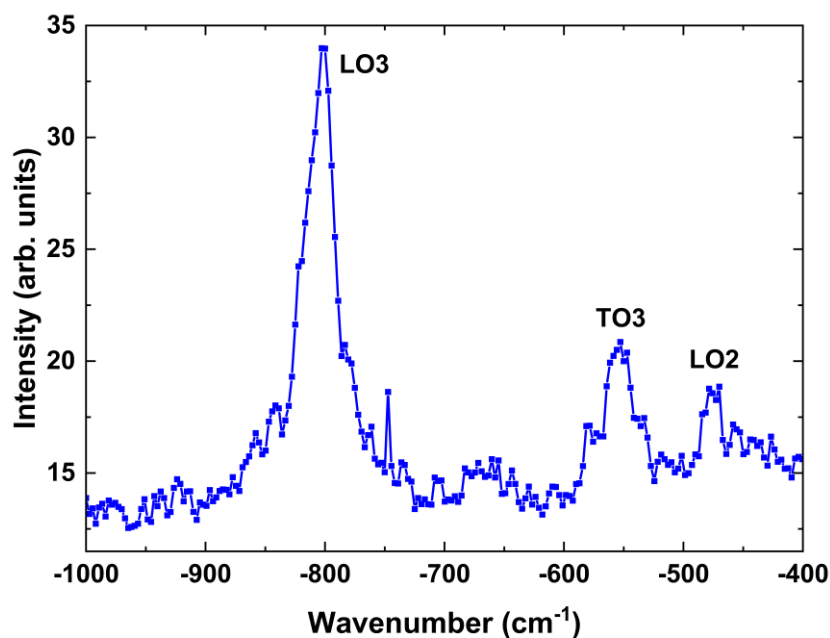


Figure 4.9. Stokes hyper-Raman scattering at 5 K, 0.1 mm spectrometer slit width (without MIR-FEL irradiation)

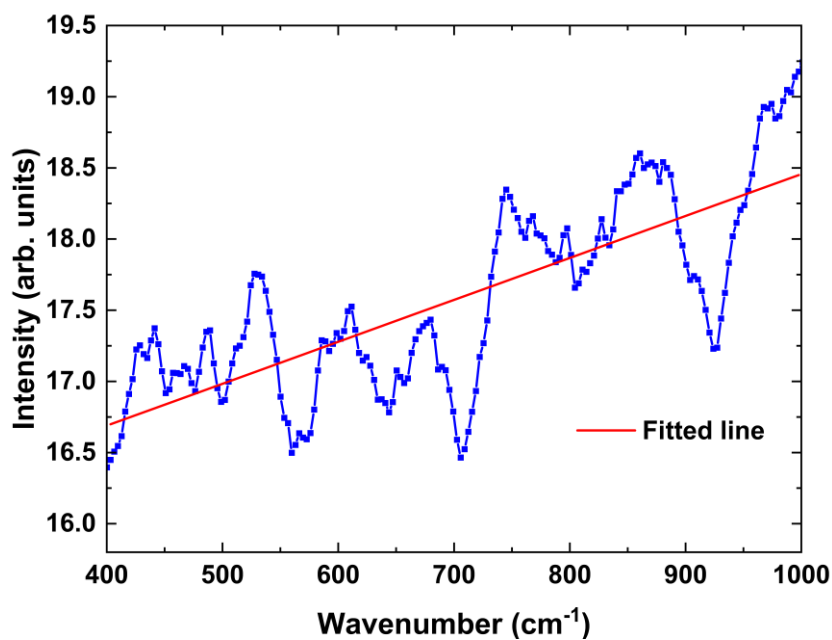


Figure 4.10 Anti-Stokes hyper-Raman scattering at 5 K, 0.1 mm spectrometer slit width (without MIR-FEL irradiation)

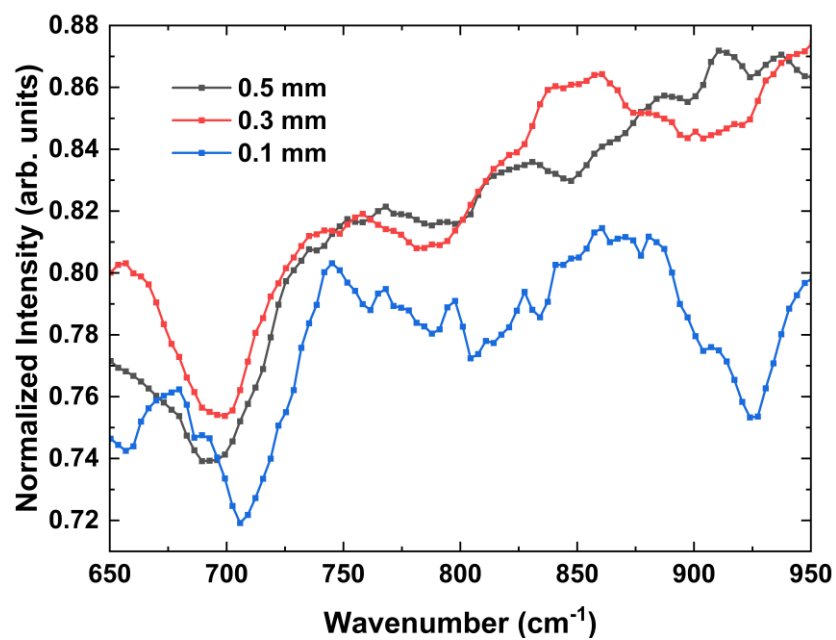


Figure 4.11. Anti-Stokes hyper-Raman scattering at 5 K, different spectrometer slit widths
(without MIR-FEL irradiation)

4.5. Selective phonon excitation via MIR-FEL irradiation

Finally, we proceed to demonstrate the selective excitation of the LO₃ phonon mode via MIR-FEL irradiation. The MIR-FEL micro pulse energy was set to $\sim 1.2 \mu\text{J}$, and that of the ps-laser was set to $\sim 830 \mu\text{J}$. The observation temperature must be maintained at cryogenic conditions to suppress thermal excitation. To achieve this, the SrTiO₃ crystal was kept at 5 K inside the cryostat. Scattered light was recorded simultaneously with MIR-FEL under both on and off conditions by driving the ps-laser at twice the MIR-FEL macro-pulse repetition rate, at 4 Hz and 2 Hz, respectively. Spectra were obtained by accumulating 200 times per point to optimize the signal-to-noise ratio. The spectrometer slit width was set to 1 mm, as narrower slits were unable to capture the low-intensity anti-Stokes HRS scattering within this experimental configuration.

We could record an anti-Stokes HRS with the peak at $\sim 761 \text{ cm}^{-1}$ with MIR-FEL irradiation. The recorded scattering band shape somewhat overlaps with the expected LO₃ phonon mode position (800 cm^{-1}), although its peak appears to be red-shifted. The spectrum bandwidth also broadens (approximately 80 cm^{-1} FWHM) with MIR-FEL irradiation at 5 K (Figure 4.12), compared to the spectrum without MIR-FEL irradiation at room temperature ($\sim 50 \text{ cm}^{-1}$ FWHM) (Figure 4.8). This bandwidth broadening might have been due to the use of a wide spectrometer slit width.

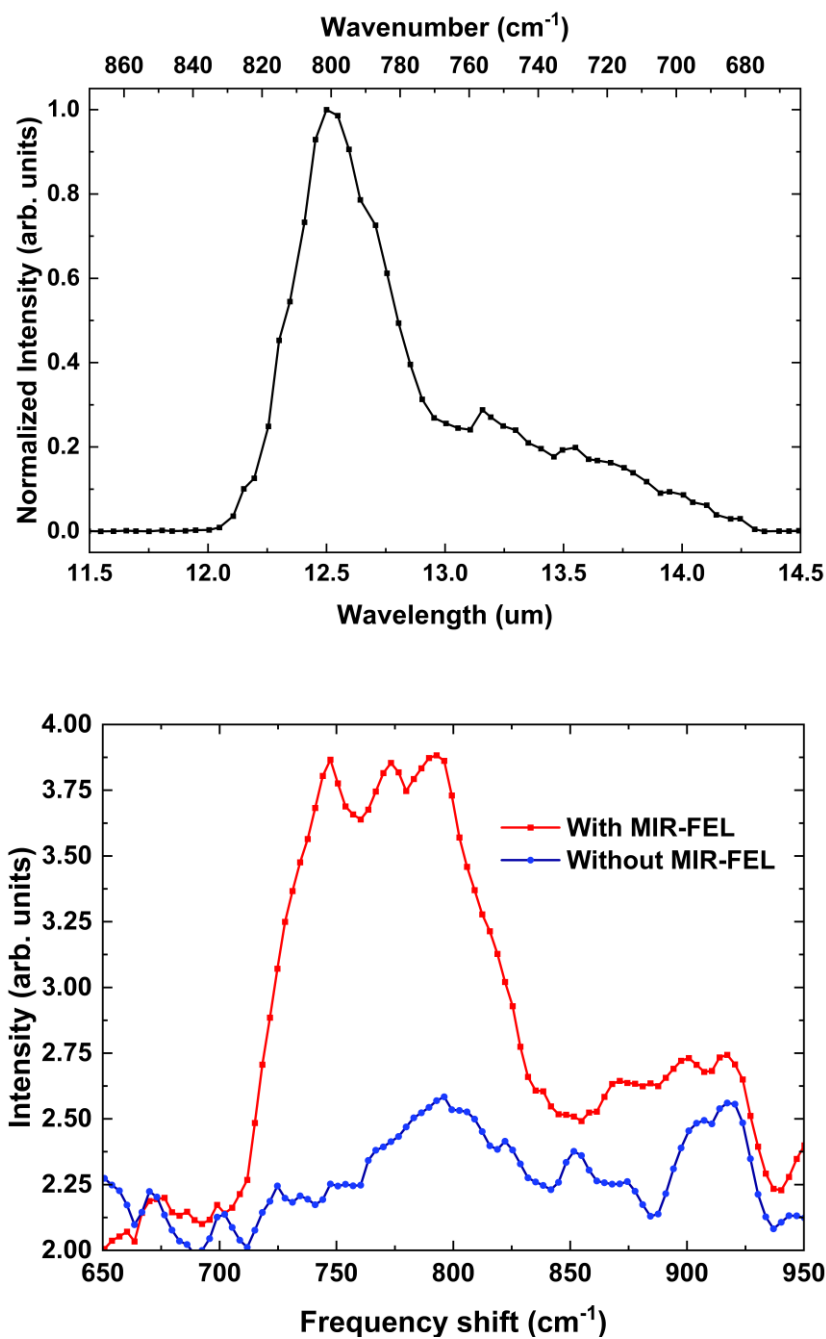


Figure 4.12. Pump MIR-FEL spectrum at 12.5 μm (800 cm^{-1}) applied to induce phonon excitation (Upper panel), Anti-Stokes hyper-Raman scattering with and without MIR-FEL irradiation at 5 K (Lower panel)

After stopping the laser injections, we observed a circular area of color variation and a black laser-damage spot on the sample surface inside the cryostat. (Figure 4.13) However, the color variation disappeared when the sample was removed from the cryostat after cooling was

stopped. Only the dark sample damage spot remains after disassembling the sample from the holder at room temperature. This color appearance is assumed to result from the color-centered effect that happens when certain crystals are heated to high temperatures. In earlier studies by Oji Sato et al. and Akasegawa et al., on the T_{2g} phonon excitation of diamond with MIR-FEL, they also observed a red shift in the spectrum along with damage caused by high-intensity laser irradiation.^{145),146)} Additionally, based on studies of the temperature dependence of $SrTiO_3$ phonon frequencies and linewidths by V. N. Denisov et al., the LO3 phonon mode exhibits only a slight frequency shift of $\sim 15\text{ cm}^{-1}$, and the LO spectrum linewidth increases by around 10 cm^{-1} (FWHM) as the temperature rises from roughly 300 K to 400 K.^{148),165)}

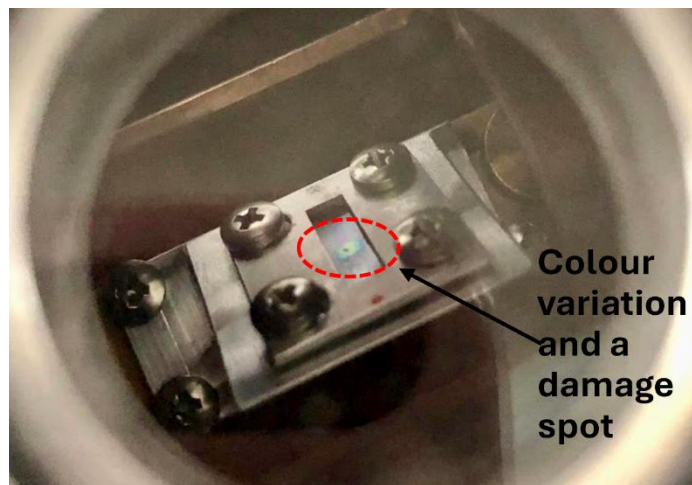


Figure 4.13. Image of the $SrTiO_3$ crystal sample inside the cryostat after the experiment

4.5.1. Spectra linewidth dependence on the spectrometer slit width



Figure 4.14. Spectral resolution measurement using a neon lamp

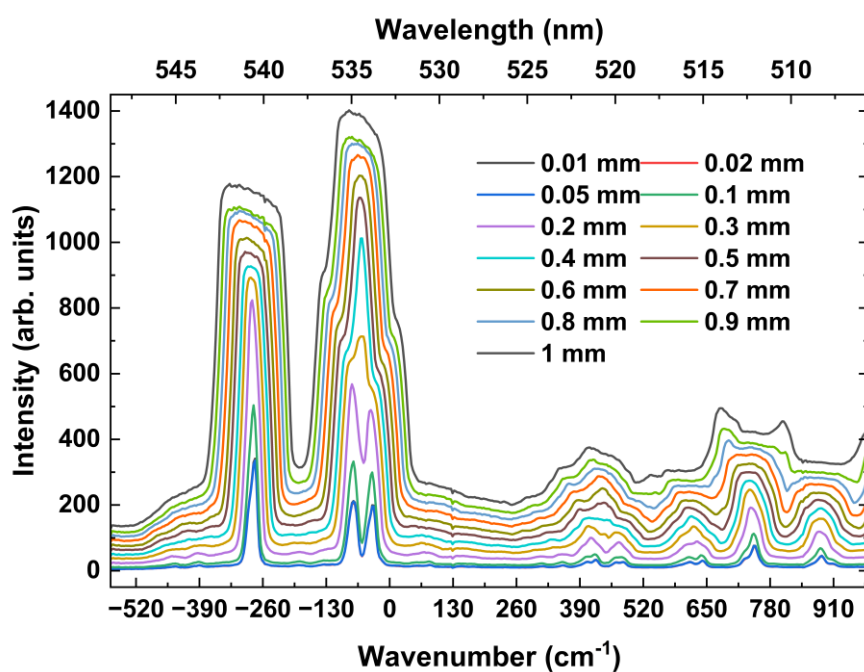


Figure 4.15. Neon light recorded with different spectrometer slit widths (shown together with wavelength)

We conducted a measurement using a neon light to observe how the spectral resolution depends on different slit widths of the spectrometer. The neon light is used to implement a preliminary step to calibrate the spectrometer because its wavelengths are already known and established. Here, we recorded light from the neon lamp at room temperature using different spectrometer slit widths ranging from 0.01 to 1 mm. The results are shown in Figure 4.15. If we focus on the spectrum at -280 cm^{-1} (which corresponds to 540 nm emission from neon light), the linewidth is approximately 20 cm^{-1} (FWHM) when measured with a 0.1 mm spectrometer slit. Increasing the slit width broadens the spectrum, where, at a 1 mm slit width, the linewidth reaches $\sim 150\text{ cm}^{-1}$ (FWHM). It is also clearly visible that the two peaks at -74 cm^{-1} (which corresponds to 534 nm emission from neon light) and -36 cm^{-1} (which corresponds to 533 nm emission from neon light) merge into a single broad peak with a linewidth of $\sim 150\text{ cm}^{-1}$ (FWHM). Based on this observation, we have verified the spectral resolution of our measurement using a 1 mm spectrometer slit width, confirming that the broadening in the anti-Stokes HRS spectrum shown in Figure 4.12 is accompanied by the use of a wider spectrometer slit.

4.6. Conclusion

We have successfully confirmed the selective excitation of the Raman-inactive LO3 phonon mode of SrTiO₃ via MIR-FEL irradiation using anti-Stokes hyper-Raman scattering spectroscopy. We observed a red-shifted, broadened anti-Stokes hyper-Raman scattering peak at around 760 cm⁻¹. These results are attributed to the wide spectrometer slit width and high-intensity laser irradiation during the observation of weak anti-Stokes scattering from MIR-FEL-induced LO3 phonon excitation. Our achievement in this observation demonstrates the ability of MIR-FEL to induce selective excitation of phonon modes, whether Infrared active or inactive, Raman active or inactive, that are within the MIR-FEL tunable range.

Chapter 4 is mainly adapted from “Bo, J.Y.H., Zen, H., Yoshida, K. et al. Observation of Selective Excitation of Raman Inactive Phonon Mode of Strontium Titanate Through Anti-Stokes Hyper-Raman Scattering Process. *J Infrared Milli Terahz Waves* **45**, 999–1009 (2024). <https://doi-org.kyoto-u.idm.oclc.org/10.1007/s10762-024-01014-8>”. (Reproduced with permission from Springer Nature)

Chapter 5

Temporal evolution of the resonant phonon-induced antiferromagnetic domain changes

5.1. Overview

Resonances, in general, provide the most energy-efficient and rapid pathway to induce modifications within condensed-matter systems. When an electromagnetic wave travels through a crystal at a frequency matching that of phonons at the Brillouin zone center (Γ -point), resonant absorption of the radiation energy via optical phonons occurs, typically within the infrared (IR) spectrum. Infrared active phonons are strongly driven at resonance and are known to modify material properties via coupled or otherwise inaccessible modes. Owing to such interactions, resonant phonon control appears to be a promising ultimate mechanism for efficient and rapid non-thermal manipulation of magnetic orders in AFM materials. One particularly intriguing question is how much phonons affect variations in magnetic order in collinear antiferromagnets, especially since other mechanisms fail to even induce such changes.

Recently, a study led by P. Stremoukhov et al. worked on addressing the interaction between AFM order in NiO and the lattice distortion induced by the IR laser pulses.²¹⁾ By introducing NiO samples with IR irradiation across the whole phononic spectral region (12.5 to 30 μm), they observed the response of domain structures before and after irradiation. Their observation revealed that transient changes in the domain patterns occur only when the resonant excitations are carried out at the frequencies of the LO and 2TO phonon modes and confirmed that the resonant excitations in the frequencies of optical phonons are indeed capable of manipulating AFM domains in NiO. The surprising findings from their study are that irradiation at strongly

infrared-absorbing TO modes results in no discernible effect on the AFM domains; however, irradiation at the infrared-inactive 2TO mode causes substantial domain displacements.

However, their observation was limited to single captures of domain images taken 100 μs after IR irradiation, and information on how the domain dynamics evolved throughout the process or how the resonantly excited phonon lifetime influences the domain recovery dynamics has not yet been discovered. Therefore, in this study, we attempted to explore the temporal evolution of the AFM domain patterns changes under resonant excitation of the 2TO phonon mode.

5.2. Spin-phonon coupling in NiO

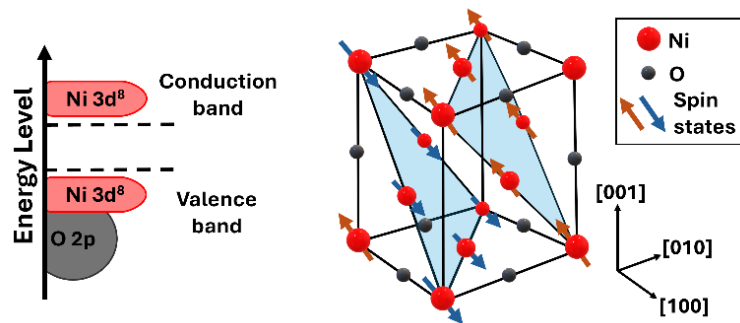


Figure 5.1. Energy band and magnetic structure of Nickel Oxide

NiO crystallizes in rock salt structure in which Ni^{2+} ions and O^{2-} anions alternate on face-centered cubic lattice. The material is a charge-transfer-type insulator, meaning that its insulating behavior arises from strong Coulomb interactions and the hybridization between Ni 3d and O 2p orbitals rather than from a simple band gap predicted by band theory.¹⁶⁶⁾ NiO belongs to the space group symmetry of $\text{Fm}\bar{3}\text{m}$ above T_N , with a lattice parameter of 4.177 Å. Below T_N , the cubic symmetry distorts slightly to rhombohedral ($\text{R}\bar{3}\text{m}$) as the material undergoes AFM ordering.¹⁶⁷⁾ The rhombohedral distortion angle is 0.09° at 5 K.¹⁶⁸⁾ As for its magnetic structure, the spins of Ni^{2+} ions, located in an octahedral construction by O^{2-} anions,

align ferromagnetically within the (111) plane and antiferromagnetically with the adjacent plane, producing a type-II AFM structure.^{83),167)}

NiO is known to exhibit rich phonon dynamics strongly influenced by its magnetic ordering. Above T_N , in the paramagnetic phase, NiO exhibits a single triple-degenerate polar mode at the Brillouin zone center (Γ -point) with F_{1u} symmetry. This F_{1u} mode is observed at a TO phonon frequency of $\sim 400 \text{ cm}^{-1}$.^{169),170)} Below T_N , the magnetic exchange interaction causes the TO mode to split into two different modes with energies polarized parallel and perpendicular to the AFM direction, $E_{\parallel}$ and $E_{\perp}$.^{167),169)} An almost temperature-independent LO mode is observed at $\sim 550 \text{ cm}^{-1}$, which softens by only about 1% at 525 K.¹⁶⁷⁾ Additionally, in the AFM phase, below T_N , a prominent second-order two-magnon (2M) excitation appears at $\sim 1500 \text{ cm}^{-1}$. It originates from two Brillouin zone (BZ) edge magnons, likely X or Z points, propagating with opposite momenta.^{171),172)} This highly intense BZ edge 2M magnon mode dominates in the Raman scattering spectra but is suppressed under ultraviolet irradiation, due to its absence in resonance, resulting from the difference in energy scales, unlike BZ center (Γ -point) phonons. The BZ edge 2M mode is strongly suppressed above T_N ; however, a study by Lacerda et al. observed that it does not disappear completely at temperatures above 600 K, suggesting fluctuations in AFM order or persistent AFM ordering.¹⁷³⁾

In rock-salt centrosymmetric crystals like NiO, the LO and TO phonons are not accessible with first-order Raman (linear Raman) Spectroscopy, unless activated by the presence of defects. However, the weak rhombohedral lattice distortion caused by the AFM ordering below T_N makes the LO and TO phonons visible in the Raman spectrum.^{171),175),176)} Phonons and magnon modes of bulk NiO crystal have been experimentally confirmed using inelastic neutron scattering spectroscopy, Raman spectroscopy, and oblique incidence infrared reflectance spectroscopy.^{173),174),176),177)} The following table shows the information on experimentally observed phonon modes of bulk NiO crystals at room temperature.

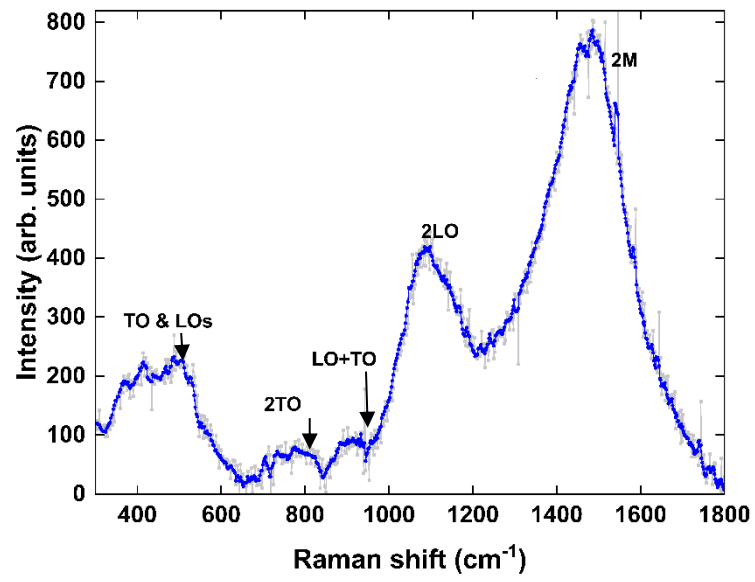


Figure 5.2. Raman spectroscopy of bulk NiO at room temperature¹⁷⁴⁾

Table 5.1. Experimentally recorded vibrational modes of Nickel Oxide (NiO)^{173),174),176),177)}

Phonon mode	Frequency	Infrared	Raman	Note
TO	~350 cm ⁻¹ to 410 cm ⁻¹	Active	Weakly active	Raman-forbidden in perfect crystals, but weakly visible in the Raman spectrum due to the weak rhombohedral distortion or the presence of defects
LO	~520 cm ⁻¹ to ~580 cm ⁻¹	Active	Weakly active	
2TO	~720 cm ⁻¹ to ~899 cm ⁻¹	Inactive	Active	-
TO + LO	~913 cm ⁻¹	-	-	-
2LO	~1100 cm ⁻¹ to ~1142 cm ⁻¹	Inactive	Active	-
2M	~1500 cm ⁻¹	Active	Active	Raman band suppressed with UV irradiation

In strongly correlated AFM materials, the spin-phonon coupling conditions can be studied via temperature-dependent Raman spectroscopies, as the coupling influences the temperature dependence of phonons, making it significantly deviated from theoretical predictions. Accordingly, the strength of spin-phonon coupling can be determined from the peak positions of phonons in the Raman spectra taken over a wide range of temperature, extending both below and above T_N . The deviation of the phonon peak position below T_N from the theoretically predicted phonon anharmonic decay curve was attributed to the influence of spin texture on phonon energies.^{176),178)–180)} The anharmonic decay dependence was derived from fitting

theoretical models to experimental data points above T_N . However, this conventional method does not work for NiO. One reason is that the LO and TO phonons are not Raman-active in rock-salt crystals; however, they appear as weak, low-intensity peaks in the Raman spectrum due to the presence of defects or a weak rhombohedral lattice distortion below T_N , which is not enough for the extraction of spin-phonon coupling strengths. Another reason is that the 2LO and 2TO bands have much higher intensity but always appear in the tail of the intense 2M magnon mode. These conditions do not allow an accurate determination of the phonon peak position for use in the spin-phonon coupling strength calculations. Furthermore, the T_N of NiO is quite high, which restricts the temperature range for anharmonic curve fitting before irreversible structural changes occur in the NiO crystal. Ayan et al.¹⁷⁶⁾ employed ultraviolet Raman spectroscopy, which suppressed the 2M scattering band and addressed the aforementioned challenges to determine the spin-phonon coupling in NiO. Ultraviolet irradiation (325 nm) is close to the optical band gap of NiO, and therefore, matching the resonant band-to-band transition increases light absorption while simultaneously enhancing the BZ center (Γ -point) phonons but eliminating the non-resonant BZ edge 2M magnon band. The figure (8) shows the room temperature Raman spectrum of NiO obtained under ultraviolet radiation. The LO, 2TO, LO TO and 2LO peaks can be clearly seen at $\sim 580 \text{ cm}^{-1}$, $\sim 738 \text{ cm}^{-1}$, $\sim 913 \text{ cm}^{-1}$ and $\sim 1142 \text{ cm}^{-1}$, respectively.¹⁷⁶⁾ And using the temperature-dependent ultraviolet Raman spectra of 2TO and 2LO modes, the spin-phonon coupling factors of the NiO phonon modes were determined from the following calculations,¹⁷⁶⁾

$$\lambda = - \frac{\omega_R(T_{low}) - \omega_A(T_{low})}{[\phi(T_{low}) - \phi(2T_N)] S^2} \quad \text{Eq. (5.1)}$$

where $\omega_R(T_{low})$ is the observed Raman peak at the lowest recorded temperature, and $\omega_A(T_{low})$ is the anharmonic prediction of that Raman peak at that temperature, $\phi(T_{low})$ quantifies spin correlation in the AFM phase at and $\phi(2T_N)$ provides no spin correlation reference in the

paramagnetic phase. Accordingly, spin-phonon coupling factors in bulk NiO are calculated as -15.7 cm^{-1} for the 2TO mode, 28.2 cm^{-1} for the 2LO mode, and correspondingly, -7.9 cm^{-1} for the TO mode and 14.1 cm^{-1} for the LO mode.¹⁷⁶⁾ This indicates that NiO exhibits exceptionally strong spin-phonon coupling compared to other AFM insulators such as MnF_2 (0.4 cm^{-1})¹⁷⁹⁾, FeF_2 (1.3 cm^{-1})¹⁷⁹⁾, and ZnCr_2O_4 (3.2 to 6.2 cm^{-1})¹⁸¹⁾, making it a distinctive feature suitable for spintronic applications. Their study also reveals that Ni spins interact more strongly with LO phonon modes than with TO phonon modes, producing opposite effects on phonon energies.

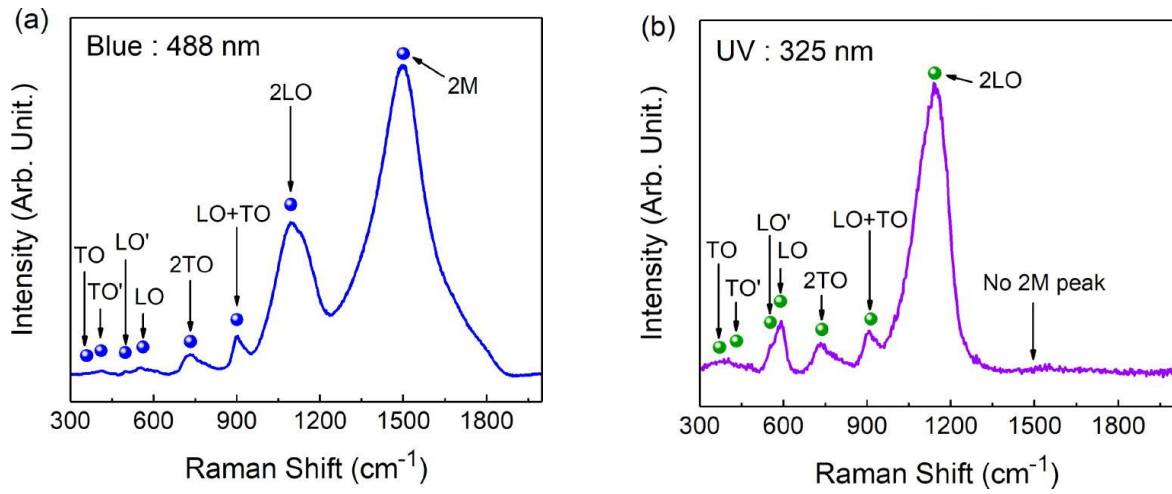


Figure 5.3. Room-temperature Raman spectra for (a) 488 nm and (b) 325 nm laser excitation¹⁷⁶⁾

5.2.1. Antiferromagnetic domains in NiO

Bulk NiO exhibits a complex magnetic domain topology that arises from the crystallographic and magnetic anisotropies of the AFM phase. Below T_N , the spins of Ni^{2+} ions in the $[111]$ planes of the rock salt structure lie ferromagnetically within the plane. Between adjacent planes, the spins alternate in opposite magnetization, forming an AFM configuration. Due to magnetic ordering, the NiO crystal structure undergoes a rhombohedral distortion along the $\langle 111 \rangle$ directions. Each orientation is so-called a twin domain (T-domain), and four possible domains form along the four equivalent $\langle 111 \rangle$ directions of $T_1 [1,1,1]$, $T_2 [1,1,\bar{1}]$, $T_3 [1,\bar{1},1]$, $T_4 [\bar{1},1,1]$.^{83),84),182),183)} These T-domains are oriented along the $\langle 112 \rangle$ directions, and therefore, within each T-domain, there form three more equivalent orientations perpendicular to that of the rhombohedral distortion. These are referred to as spin domains (S-domains).^{83),84),142),182)–184)} Accordingly, 12 domain types are present in AFM NiO, whereas the total count would increase to 24 if spin-reversal domains are taken into account. The 12 orientational bulk AFM domains of NiO are described in the Table 5.2.

Table 5.2 Crystallographic directions of T-domains and S-domains in bulk NiO^{182),183)}

T-domains		T_1	T_2	T_3	T_4
		$[1,1,1]$	$[1,1,\bar{1}]$	$[1,\bar{1},1]$	$[\bar{1},1,1]$
S-domains	S_1	$[\bar{2},1,1]$	$[2,\bar{1},1]$	$[2,1,\bar{1}]$	$[2,1,1]$
	S_2	$[1,\bar{2},1]$	$[\bar{1},2,1]$	$[1,2,1]$	$[1,2,\bar{1}]$
	S_3	$[1,1,\bar{2}]$	$[1,1,2]$	$[\bar{1},1,2]$	$[1,\bar{1},2]$

T-domains in NiO can be observed using polarized light microscopies due to their significant birefringence ($\Delta n \sim 0.003$), which arises from the rhombohedral distortion.⁸³⁾ In contrast, the optical birefringence associated with S-domains is minimal, two orders of magnitude smaller

than that of the T-domains.^{83),182),183)} Therefore, S-domains do not measurably affect the polarization of the propagating light, and advanced optical techniques are required in order to visualize them. In this study, AFM domains in NiO will be visualized by the MOB technique in transmission geometry using linearly polarized light. Since S-domains have insignificant influence on the polarization of the propagating light, they are negligible in our observations. The AFM domains we further refer to and analyzed in our observations are primarily T-domains.

5.3. Experimental Configuration

A NiO substrate (Crystal Base Co., Ltd.) with a (100) plane orientation was used as our target sample. The crystal was grown by the floating-zone crystal growth method, yielding a high-quality crystal with 99.9% purity. The sample substrate was polished on both sides to enhance light transmission by minimizing scattering and interference effects arising from rough or uneven surfaces. The dimension of the NiO sample was 5 mm × 5 mm and 0.3 mm in thickness. The sample was placed on the customized sample holder, normal to the probe laser beam path. To visualize the AFM domain patterns, the sample is illuminated using a linearly polarized probe light of wavelength 532 nm, which is generated by an actively Q-switched ns-Nd:YAG laser (Surelite-II-10, Amplitude Laser Inc.) with a second harmonic generation module in the KU-FEL facility. To perform resonant phonon excitation of the optical phonon mode in NiO, MIR-FEL with a central wavelength of 13.5 μm (photon energy of 92 meV), which corresponds to the 2TO phonon mode wavelength, was employed. An off-axis parabola (OAP) with a hole was positioned before the sample holder. The MIR-FEL beam was focused onto the sample surface by reflecting from the OAP surface, while the ns-Nd:YAG laser passed through the hole of the OAP and incident on the sample surface. The estimated ns-laser beam spot size on the sample was ~150 μm in diameter, while the MIR-FEL beam spot was managed to cover the entire image observation area, 250 x 187 μm². The spatial overlapping of these two lasers

was achieved by adjusting the OAP's tilt angle, and temporal overlap was controlled via electric trigger signals. An optical delay stage was employed in the ns-laser path to control the timing delay with respect to MIR-FEL irradiation. The transmitted light then passes through a short-pass filter of 700 nm, which eliminates any unwanted scattered light. An objective lens with 20 $\times$ magnification was attached to be able to capture the microscopic AFM domain patterns. An analyzer was also employed in the transmission path to confirm the polarization of the transmitted light. A CMOS compact scientific camera (acA720-290gm, Basler) by a tube lens (MT-1, Mitutoyo) having a focal length of 200 mm, was used to record the images.

Macro pulses of MIR-FEL with ~ 4 μ s (FWHM) pulse duration and 2 Hz repetition rate, and a ns-Nd:YAG laser with 4 ns (FWHM) pulse duration and 2 Hz repetition rate were employed in this observation. The wavelength of the ns-laser was 532 nm, and that of MIR-FEL was tuned to 13.5 μ m to match the 2TO phonon frequency of NiO. The probe ns-laser had an intensity of ~ 10 μ J, while the MIR-FEL was set to ~ 5 mJ, delivering a beam fluence of roughly 10 J/cm² on the sample surface. The timing delay of the ns-laser relative to the MIR-FEL was controlled via a digital delay generator (DG645, Stanford Research System) using electric triggering signals. The observation was conducted at room temperature.

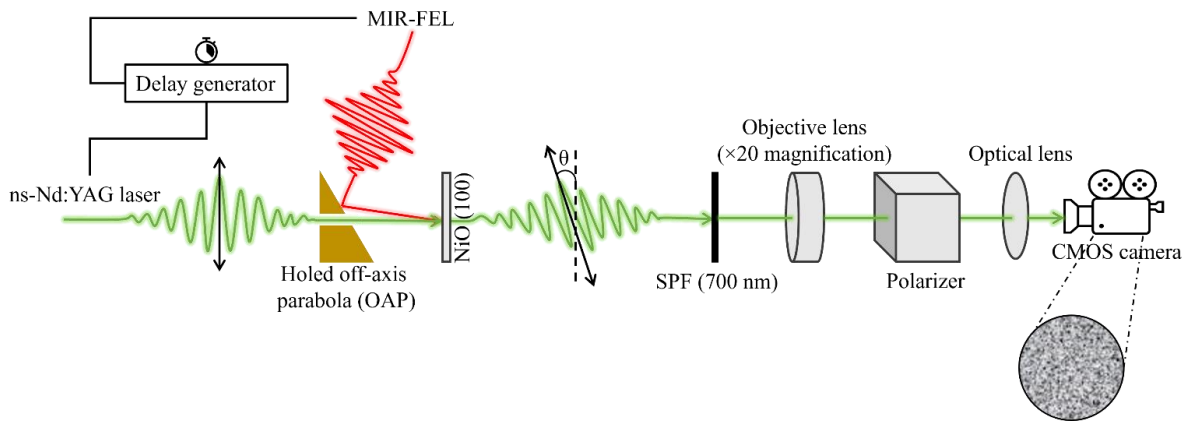


Figure 5.4. Experimental setup for imaging antiferromagnetic domain pattern dynamics¹⁷⁴⁾

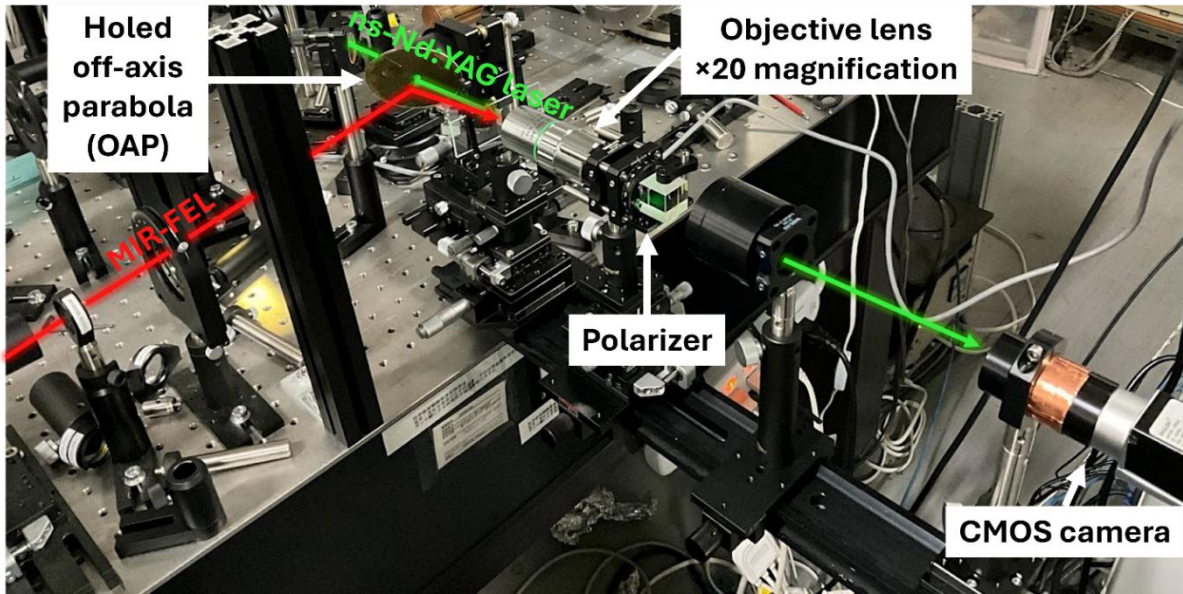


Figure 5.5. Image of the experimental setup

5.4. AFM domain pattern observation without external excitation

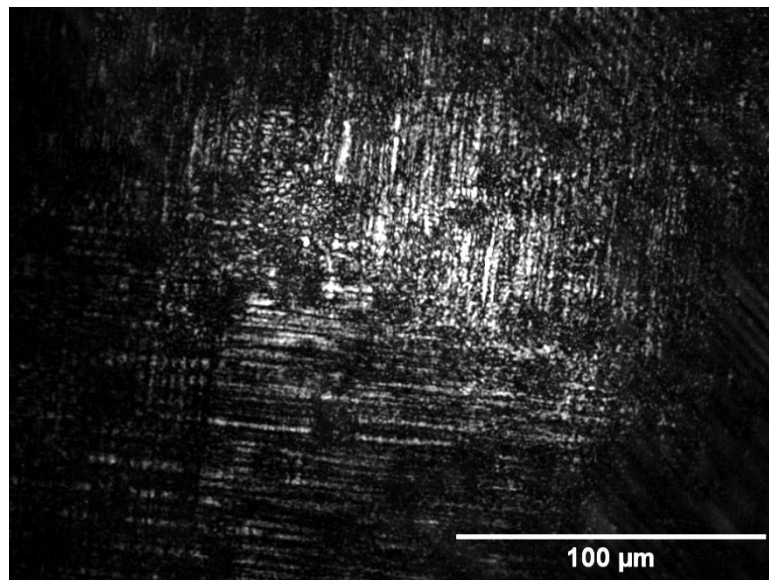


Figure 5.6. Image of the AFM domain patterns in NiO (100) single crystal, size (250 x 187)

μm^2

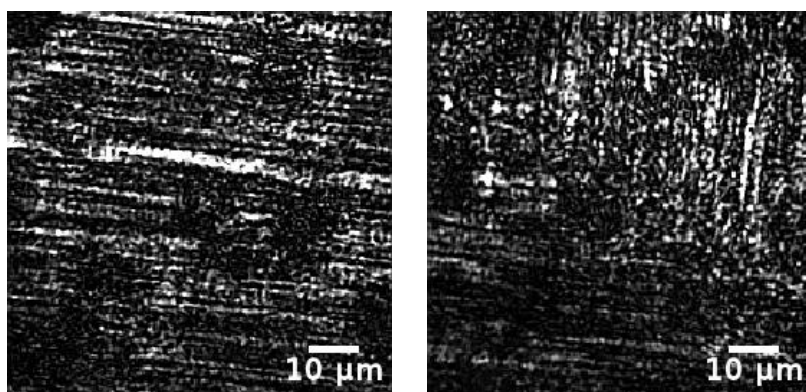


Figure 5.7. Zoom-in images of the AFM domain patterns taken from different spots in the same sample under the same experimental conditions. The size of the images is ($75 \mu\text{m} \times 75 \mu\text{m}$).

First of all, we illuminate the NiO sample surface with the ns-laser to visualize the AFM domain patterns with zero magnetic field and external excitation at room temperature. The images were captured via the event of magneto-optical birefringence in transmission geometry as shown in Figure 5.4. Figure 5.6 shows the whole observation area of the image of the AFM

domain pattern recorded, and Figure shows the 2.5 times zoomed-in and cropped images for more distinct visualization. The white and black stripes formed as alternating high- and low-contrast regions corresponding to AFM domains with different spin orientations relative to the incident polarized light. The black spots scattered across the image are due to defects (non-magnetic foreign impurities). The overall domain patterns appear as parallel clusters of stripes. Depending on the point of observation of the sample, groups of clusters oriented at 90° to neighboring groups can also be seen, as in Figure 5.6. The estimated widths of the domain stripes are up to $\sim 2 \mu\text{m}$, while their length varies. This observation is also in agreement with the sample crystalline structure and previous findings.²¹⁾

5.5. AFM domain pattern observation with MIR-FEL irradiation

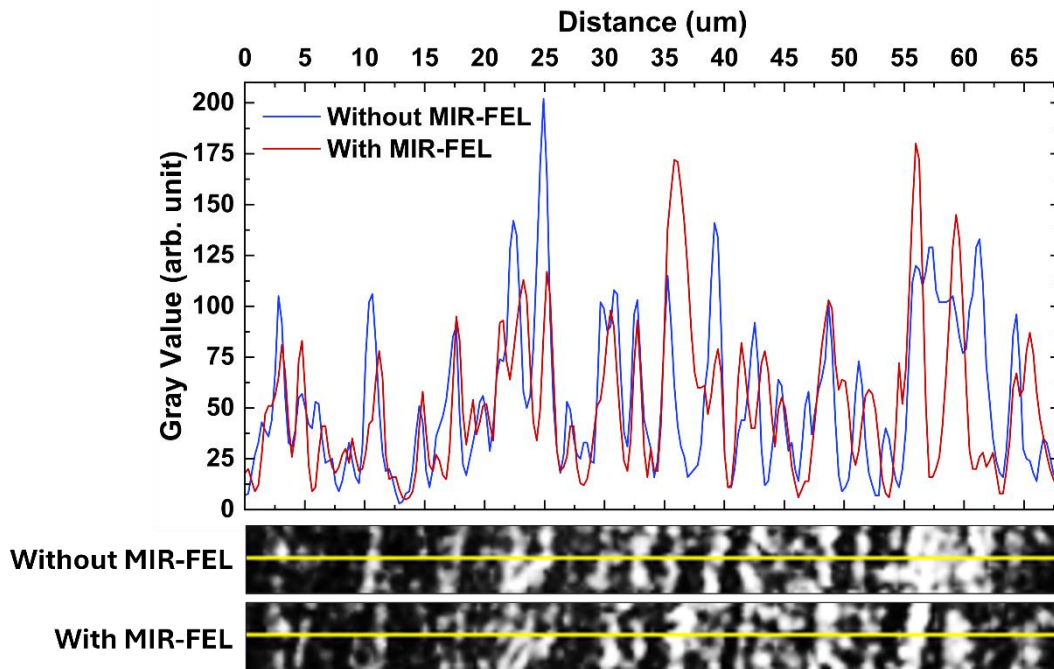
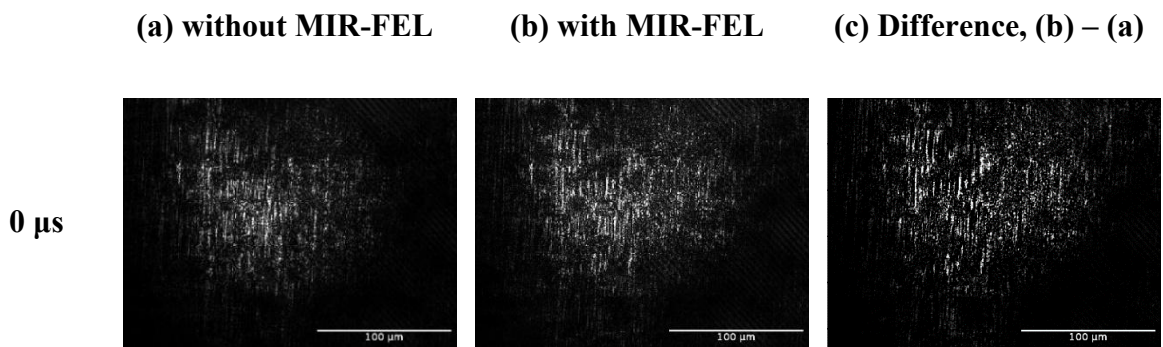


Figure 5.8. Line profile from a section of the recorded images showing the variation of the domain pattern without and with MIR-FEL irradiation. (The yellow line indicates the location from which the line profile data is extracted)

We then proceed to resonantly excite the 2TO phonon in NiO by irradiating the NiO sample with MIR-FEL tuned to the 2TO phonon wavelength ($13.5 \mu\text{m}$). The relative timing of the

pump MIR-FEL and the probe ns-laser is arranged to overlap and be synchronized, and images are recorded with both, without irradiation and with MIR-FEL irradiation conditions. Figure 5.8 shows a section from the recorded images indicating how the stripes change from no external excitation to resonant 2TO phonon excitation via MIR-FEL irradiation. Based on this observation, we noticed shifts, growth, and alternation between low and high regions of the stripes. This signifies that the AFM order within the NiO sample changes in response to the resonant 2TO phonon excitation.

Then we adjust the relative timing of the probe ns-laser from the overlapping condition with the pump laser to a delay of up to 20 ms. For each timing delay stage, images are captured similarly to the method described above. Figure 5.9 displays AFM domain pattern images in NiO (100), taken without MIR-FEL irradiation, at the time of irradiation, overlapping condition (0 μ s), and after irradiation at probe delays of 10 μ s, 100 μ s, 1000 μ s, and 10,000 μ s. The differences between the images with and without MIR-FEL irradiation are shown in row (c), where shifts in the high- and low-contrast regions are clearly visible. This highlights the significant impact of resonant 2TO phonon excitation on antiferromagnetic domains. The changes persisted for thousands of microseconds and gradually diminished over time. As the probe delay increases, the images with and without MIR-FEL become increasingly similar, eventually appearing almost identical after a 10 ms delay. This suggests that no further domain changes occur around this time and that the system has returned to its original magnetic state.



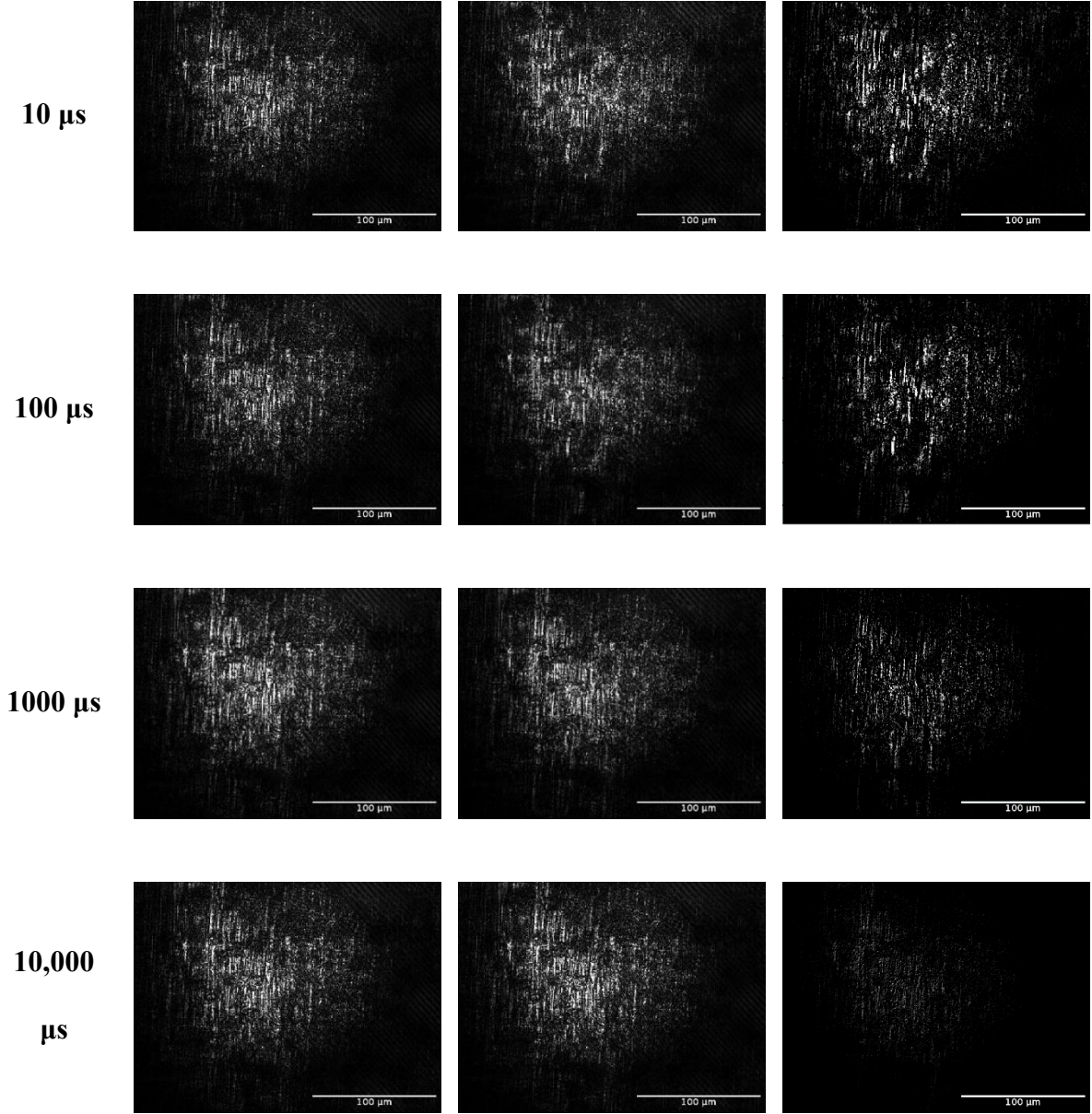


Figure 5.9. AFM domain pattern changes in NiO (100) due to resonant 2TO phonon mode excitation, along with extensive probe delay conditions (0 to 10,000 μs), (a) Domain pattern images recorded without MIR-FEL irradiation, (b) with MIR-FEL irradiation, and (c) the difference images, respectively. All images are of size (250 x 187 μm)

5.6. Structural Similarity Index Measure (SSIM)

Since qualitative analysis of domain patterns and their dynamics based solely on human insights is challenging, we employed the Structural Similarity Index Measure (SSIM)^{185),186)} to

analyze the recorded images. This method was developed in the early 2000s by Wang et al. to replace subjective evaluation methods, which are often inconvenient, time-consuming, and may not always yield fully reliable conclusions. SSIM is an objective image quality metric that measures the similarity between an original (full-reference) image and a distorted (compared) image. Two other popular conventional metrics that also employ full-reference comparison analysis are the peak signal-to-noise ratio (PSNR) and the mean squared error (MSE). They are widely used because they are simple to calculate, have straightforward physical interpretations, and are mathematically convenient for optimization. However, they are often inconsistent and less sensitive compared to the human visual system, and can assign the same value to two completely different distorted images, even when one image is more comprehensible than the other.^{187),188)} SSIM has been designed specifically to better align with human visual perception than the traditional pixel-based metrics, such as PSNR and MSE. Additionally, SSIM analysis offers a more robust and reliable method for distinguishing visually similar images with greater accuracy and sensitivity. This makes SSIM particularly suitable for use in this study, where detecting small distortions in domain patterns is crucial. This SSIM method compares two images and evaluates image degradation as perceived changes in three components: luminance (l), contrast (c), and structure (s). Suppose x and y are local matrices from the same location of the two images that are being compared, then the similarities of l , c , and s are measured as

$$\text{Luminance comparison: } l(x,y) = \frac{2\mu_x \mu_y + c_1}{\mu_x^2 + \mu_y^2 + c_1} \quad \text{Eq. (5.2)}$$

$$\text{Contrast comparison: } c(x,y) = \frac{2\sigma_x \sigma_y + c_2}{\sigma_x^2 + \sigma_y^2 + c_2} \quad \text{Eq. (5.3)}$$

$$\text{Structure comparison: } s(x,y) = \frac{\sigma_{xy} + c_3}{\sigma_x \sigma_y + c_3} \quad \text{Eq. (5.4)}$$

where μ_x and μ_y are the pixel means, σ_x and σ_y are the sample variances, and σ_{xy} is the sample covariance. C_1 , C_2 , and C_3 are small constant values to avoid numerical instability when μ_x^2 , μ_y^2 , σ_x^2 , σ_y^2 and $\sigma_x \sigma_y$ are very close to zero. The combined SSIM value can be described as

$$SSIM(x,y) = [l(x,y)]^\alpha \cdot [c(x,y)]^\beta \cdot [s(x,y)]^\gamma \quad \text{Eq. (5.5)}$$

$\alpha > 0$, $\beta > 0$, and $\gamma > 0$ are parameters used to adjust the relative importance of the three l , c , and s components. In practice, $\alpha = \beta = \gamma = 1$ and $C_3 = \frac{C_2}{2}$ are used for the most simplified version in this study. This results in

$$SSIM(x,y) = \frac{(2\mu_x \mu_y + C_1)(2\sigma_{xy} + C_2)}{(\mu_x^2 + \mu_y^2 + C_1)(\sigma_x^2 + \sigma_y^2 + C_2)} \quad \text{Eq. (5.6)}$$

SSIM ranges from 0 to 1, where 1 indicates perfect similarity (identical images), and 0 indicates complete difference between the comparison images. The SSIM method satisfies the following conditions:

- (1) SSIM is symmetric: $SSIM(x,y) = SSIM(y,x)$
- (2) It is bounded: $SSIM(x,y) \leq 1$
- (3) And can achieve a unique maximum value: $SSIM(x,y) = 1$, if and only if $x = y$.

5.6.1. Results from SSIM analysis

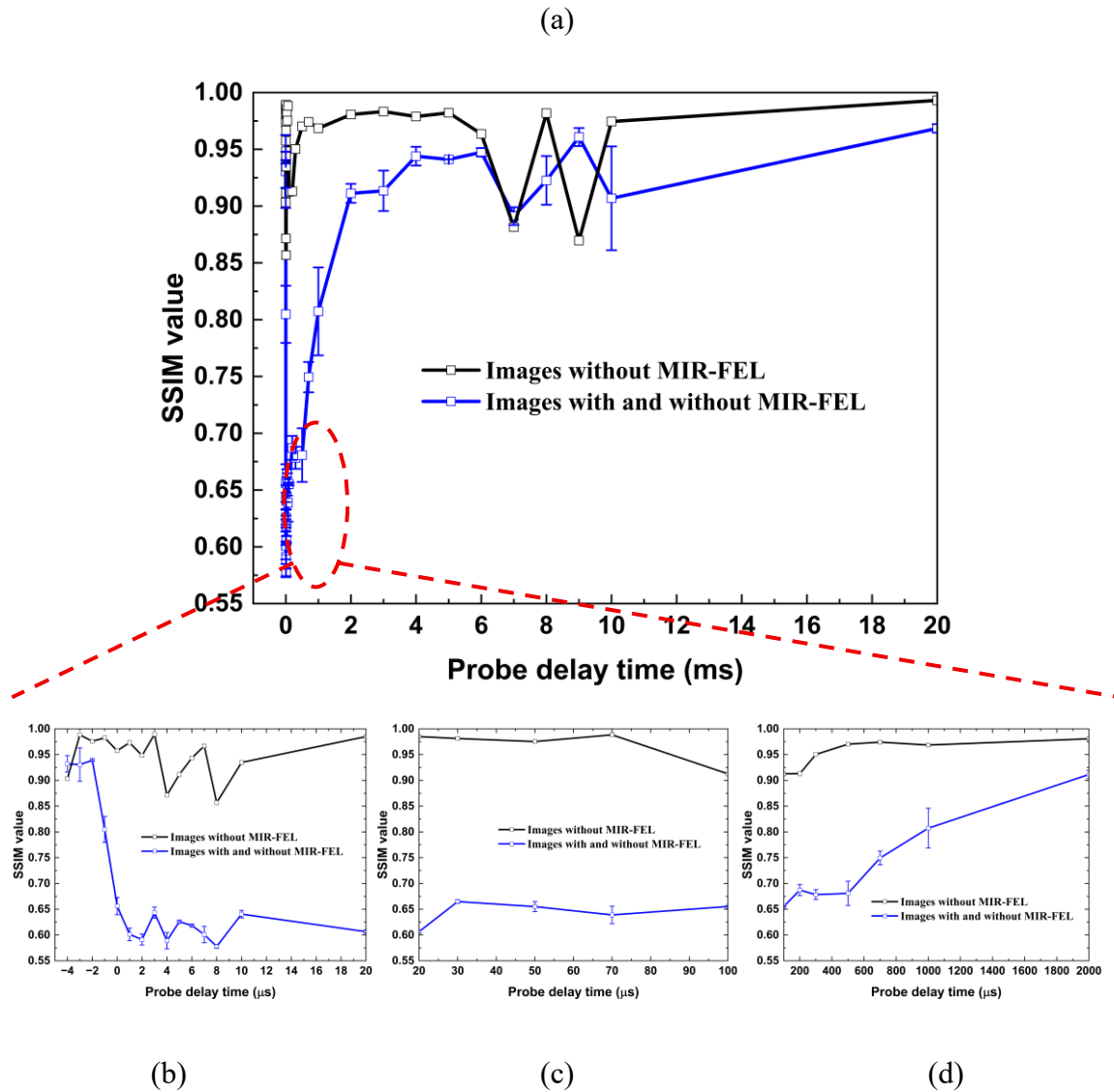


Figure 5.10. SSIM value of AFM domain images. (a) probe delay time up to 20 ms, (b) probe delay time from -4 to 20 μ s, (c) probe delay time from 20 to 100 μ s, (d) probe delay time from 100 to 2000 μ s. The black line represents the comparison of images from two trials without MIR-FEL irradiation, and the blue line represents the comparison of images obtained without and with MIR-FEL irradiation

For this study, the SSIM metric was implemented in the LabVIEW VI program to evaluate the similarity of recorded images. We input the image recorded without MIR-FEL irradiation as the original (full-reference) image and the images with MIR-FEL irradiation as the distorted

(compared) images. The resulting SSIM values for each probe delay time, ranging from ($-4\ \mu\text{s}$ to $20\ \text{ms}$), are plotted in blue line in Figure 5.10 (a). Figure 5.10 (b-d) shows the early-stage conditions from $-4\ \mu\text{s}$ to $2000\ \mu\text{s}$. We then also compare the images recorded without MIR-FEL irradiation at each probe delay stage, the results of which are also plotted in black line in the Figure 5.10. These results evidently show the MIR-FEL-induced changes in the AFM domain images. The variation in SSIM values observed here may seem modest owing to the relatively smaller microscopic domain dynamics compared to the observation area. This can be enlarged by measuring the local SSIM values of smaller regions or by using an objective lens with higher magnification. In this case, we will mainly focus on the fluctuation rate and timeline rather than the reduction in value. The early-stage gradual decline, seen in Figure 5.10 (b) during probe delay from around -2 to $+2\ \mu\text{s}$, is due to our MIR-FEL pulse profile, which has a $\sim 4\ \mu\text{s}$ pulse width. This spontaneous decline reflects instantaneous domain pattern changes in response to the MIR-FEL irradiation. The SSIM value then remains similar, with minor fluctuations, throughout the probe delay timeline up to $\sim 600\ \mu\text{s}$, after which a gradual inclination was observed. Eventually, the images recover to a resemblance state, achieving a high SSIM value (~ 0.9) as time progresses to $\sim 2000\ \mu\text{s}$.

We then proceeded to evaluate the three factors of SSIM (luminance, contrast, and structure) individually in order to determine which factor primarily influences the SSIM results. In a manner similar to above, the overall result, showing the full range, is presented in Figure 5.11 (a), and the close-up early stages are presented in Figure 5.11 (b-d). The luminance factor is shown by the green line, the contrast by the red line, and the structure by the black line. The results show that in terms of luminance and contrast, the AFM domain images with and without MIR-FEL irradiation remain highly consistent (SSIM value ~ 1), with only minor fluctuations over time. This suggests that the small variation in probe laser intensity during the measurement has a negligible impact on the overall domain pattern records. Meanwhile, the structure factor

of the domain images (represented by the black line) shows a high degree of similarity at the beginning of irradiation but then declines significantly, indicating the emergence of noticeable structural differences. This also remained relatively stable with slight fluctuations throughout the probing delay time, before showing a gradual incline from $\sim 600 \mu\text{s}$. From these results, it is evident that the structural factor dominates the overall SSIM value.

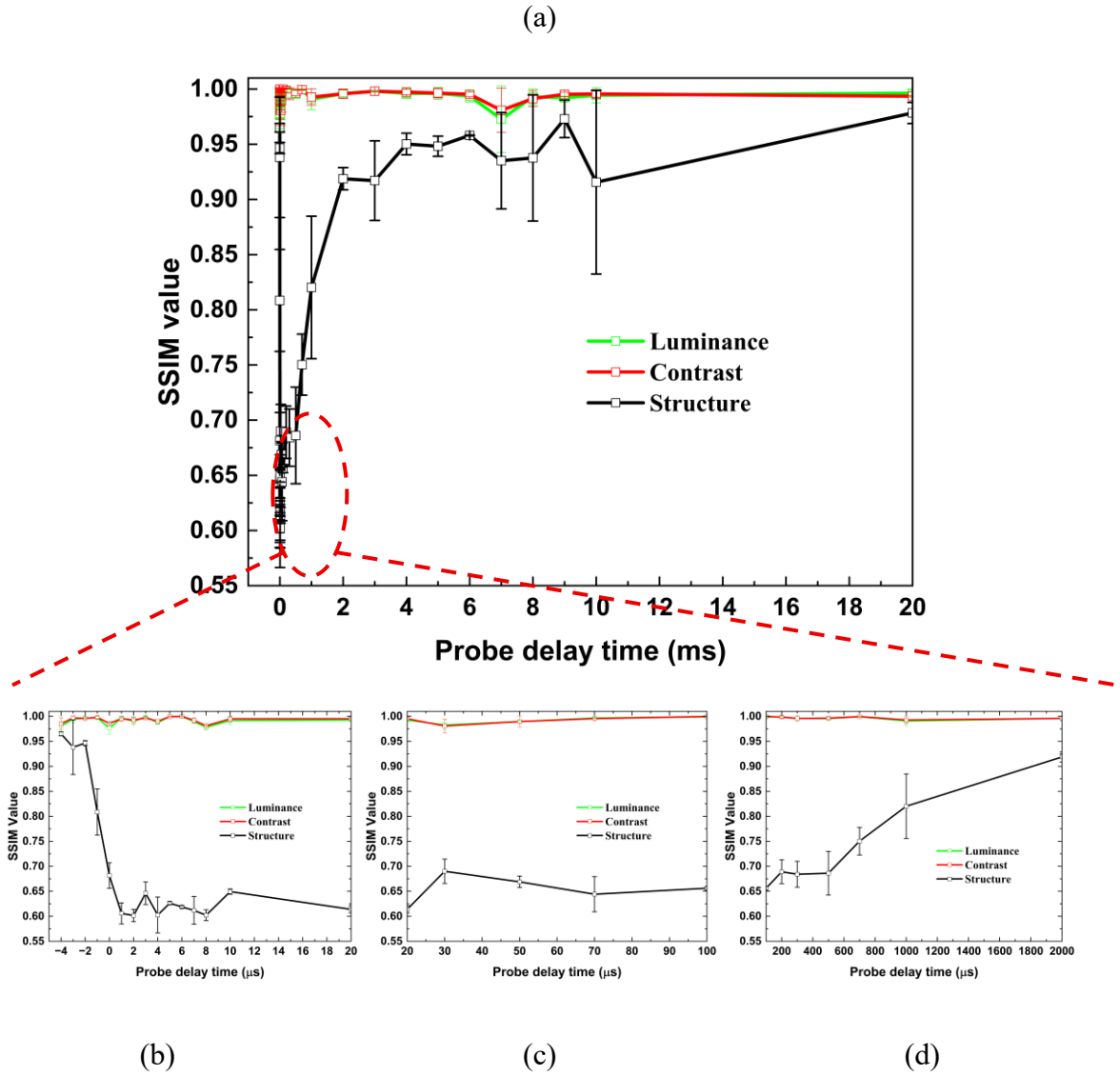


Figure 5.11. SSIM value of AFM domain images (accessing luminance, contrast, and structure factors separately). (a) probe delay time up to 20 ms, (b) probe delay time from -4 to 20 μs , (c) probe delay time from 20 to 100 μs , (d) probe delay time from 100 to 2000 μs . The black line represents the comparison of images from two trials without MIR-FEL irradiation, and the blue line represents the comparison of images obtained without and with MIR-FEL irradiation

5.7. Conclusion

From these observations, it is noted that the recovery of image similarity occurs gradually rather than abruptly. The recovery follows an exponential pattern with a time constant of $\sim 1.4 \pm 0.2$ ms. Therefore, we could conclude that the phonon-induced domain pattern changes, mediated via MIR-FEL irradiation, persisted for hundreds of microseconds and recovered exponentially at a millisecond timescale. However, the optical phonon excitations and phonon lifetime last from picoseconds to nanoseconds.^{189)–193)} Accordingly, this magnetic-state recovery period might not be solely determined by phonons. Furthermore, infrared irradiation could have increased the sample's temperature. Although earlier wavelength-dependent studies have shown that changes in magnetic domains are primarily driven by phonon excitation rather than by temperature increases, this magnetic-state recovery period might not be solely determined by phonons.²¹⁾

Chapter 5 is mainly adapted from “Ju Yoon Hnin Bo et al, “Measurement of temporal evolution of antiferromagnetic domain change in nickel oxide driven by 2TO phonon mode excitation via pump-probe experiment”, 2024 Jpn. J. Appl. Phys. **63** 112001. , DOI: 10.35848/1347-4065/ad879c”.

Chapter 6

Mode and temperature dependency of phonon-induced AFM domain recovery dynamics

6.1. Overview

In bulk NiO, the spins and optical phonons are coupled with sufficiently strong interaction that the phonon energies and thermal transport significantly deviate from the assumptions established from nonmagnetic conditions.^{107),176)} Ultraviolet Raman spectroscopy combined with ab initio calculations quantified the spin-phonon coupling for the zone-center LO and TO modes, revealing that Ni^{2+} spins couple more strongly to LO phonons than to TO phonons. The Ni^{2+} spins are found to harden the LO modes and soften the TO modes, leading to opposing spin-phonon coupling effects.¹⁷⁶⁾ The coupling coefficients are -15.7 cm^{-1} for the 2TO mode and $+14.1 \text{ cm}^{-1}$ for the LO phonon mode.¹⁷⁶⁾ Using narrow-band mid-IR pulses tuned across the phonon spectrum ($12.5\text{-}30 \text{ }\mu\text{m}$, $800\text{-}330 \text{ cm}^{-1}$), Stremoukhov et al. showed that resonant excitation of LO phonon and 2TO phonon modes in NiO produces sizable, transient displacements of the magnetic domains, while excitation at the strongly absorbing IR-active TO phonon led to minimal response.²¹⁾ Based on our previous experimental observations, it was noted that the alterations in the AFM domain pattern caused by resonant 2TO phonon excitation persisted for milliseconds before reverting to their initial states.¹⁷⁴⁾ This, neither rapid nor permanent behaviour, led to further investigations into the changes induced by resonant LO phonon excitation. Furthermore, the optical birefringence studies in NiO showed that the AFM domain structures can be merged, displaced, and irreversibly reorganized through

the application of stresses, external fields, and thermal influences.^{83),184),194)} Accordingly, it is as well crucial to investigate the influence of temperature on the resulting domain dynamics. In this study, we analyzed the comparison of different phonon modes and different observation temperatures concerning the domain recovery dynamics from time- and temperature-resolved MIR-FEL-driven resonant phonon excitations, 2TO and LO modes.

6.2. Experimental Configuration

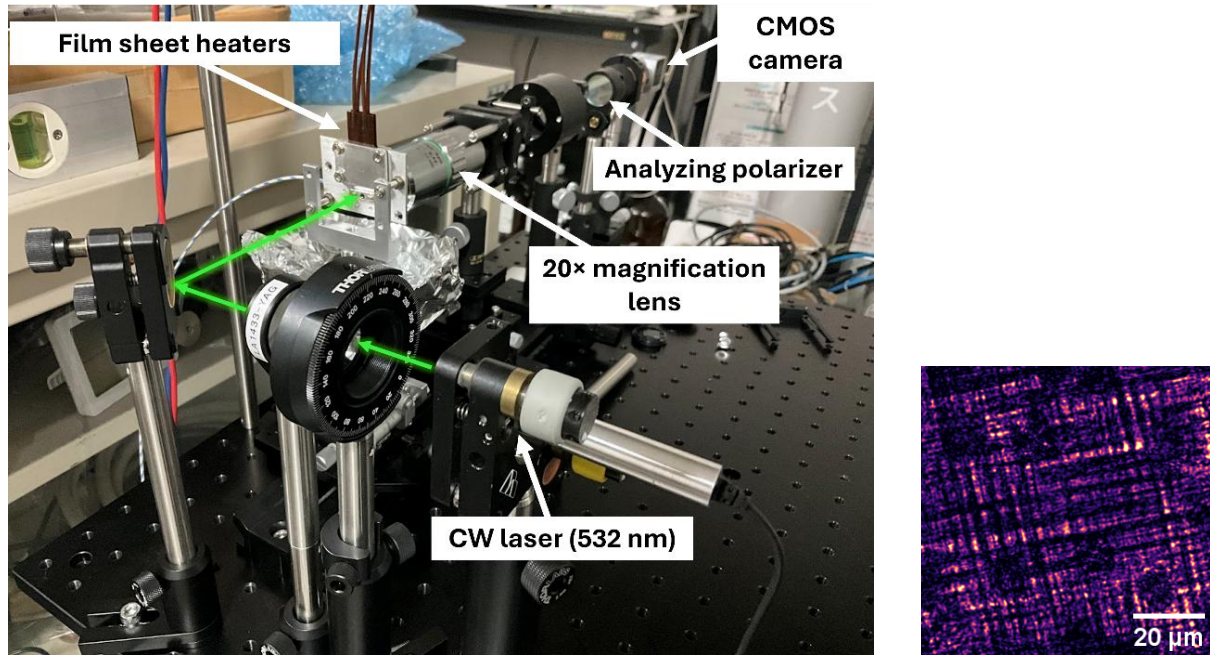


Figure 6.1. (left) Experimental setup with CW laser, (right) Image of AFM domain patterns using a CW laser at room temperature (Colored the image recorded to enhance conception)

Film-sheet heaters were clamped on each side of the sample holder to heat the NiO sample from Room temperature up to 523 K (T_N of NiO). We first employed a linearly polarized CW laser (532 nm) to obtain domain images at varying temperatures, without any external excitation (as shown in Figure 6.1.). Then, we implemented the MIR-FEL and a linearly polarized ns-Nd:YAG laser (Q-switched, Surelite-II-10, Amplitude Laser Inc.) from the KU-FEL facility to carry out the pump-probe measurements of specific resonant excitation. MIR-FEL was first tuned to a central wavelength of 13.5 μm, with macro pulse intensity of ~5 mJ,

to induce resonant 2TO phonon excitation, then to $17.15\ \mu\text{m}$, with macro pulse intensity of $\sim 1.5\ \text{mJ}$, to induce LO phonon excitation. The ns-laser has a wavelength of $532\ \text{nm}$, a pulse repetition rate of $2\ \text{Hz}$, and a pulse intensity was tuned at $\sim 15\ \mu\text{J}$. The relative timing between the two lasers was managed using a digital delay generator, with the probe ns-laser delay set up to $5\ \text{ms}$ after MIR-FEL irradiation to investigate the domain recovery dynamics. The pump-probe measurement setup is shown in Figure 6.2. The monochromatic CMOS compact scientific camera (acA720-290gm, Basler), with a tube lens (MT-1, Mitutoyo) and a focal length of $200\ \text{mm}$, gives images of size $(250 \times 187\ \mu\text{m}^2)$. Zoomed-in, colorized images are also presented in this discussion to improve visualization and understanding.

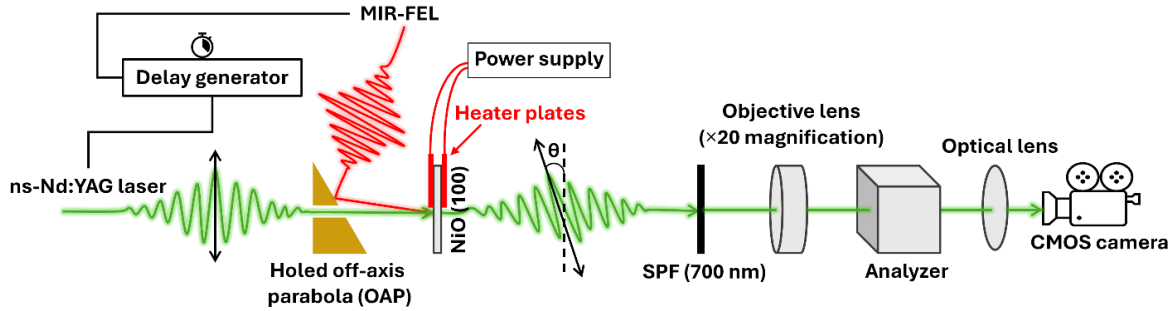


Figure 6.2. Experimental setup for imaging temperature-dependent antiferromagnetic domains

6.3. AFM domain visualization throughout the temperature increment

When the material is heated, it gradually becomes isotropic, and the birefringence disappears at T_N . Upon cooling, the birefringence of AFM domains gradually reappears.⁸³⁾ Therefore, to initially verify the magnetic birefringence in our NiO sample, AFM domain images and their contrast variations were recorded using the CW laser. Heating up was carried out using film-sheet heaters, and a K-type thermocouple monitored its temperature. (as shown in Figure 6.2.)

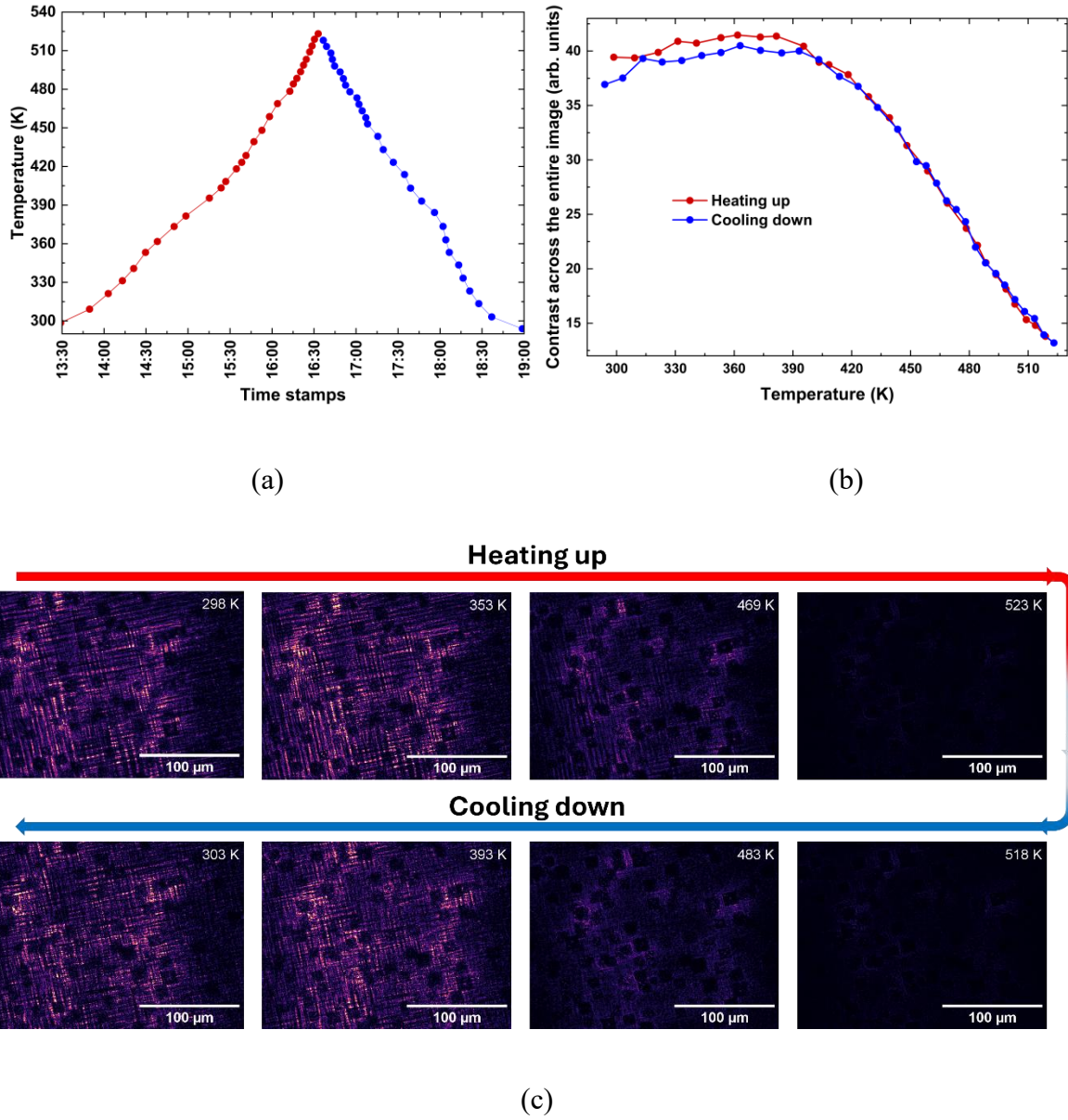


Figure 6.3. (a) Record of sample temperature throughout heating up and cooling down, (b) Contrast variation across the entire image during the temperature cycle, (c) Domain images (birefringence) acquired throughout the temperature cycle, Images of size ($250 \times 187 \mu\text{m}^2$)

With increasing temperature, the image contrast diminishes until the patterns completely disappear near 523 K, although spot defects remain faintly visible. As the sample is cooled back to room temperature, the patterns reappear, and their contrast increases. The reappearing pattern configurations appear to be somewhat different from those observed before the disappearance. This is because, as the sample is heated beyond T_N , the previous domain

configuration is erased as the system enters a paramagnetic state. Then the domains reform during the cooling process, slightly different from before the temperature cycle, as the defects and local entropy affect the reconfiguration, often leading to smaller or fragmented domain patterns.^{195),196)} However, aside from minor shifts in image positions caused by thermal expansion of the sample holder (aluminum alloy with thermal coefficient of $\sim 23 \mu\text{m}/^\circ\text{C}$), no other changes, such as shifts, growths, or shrinkages, in the AFM domain patterns were observed across the temperature variation, below T_N . These observations confirm that the observed patterns originate from AFM ordering rather than surface morphology, thereby confirming the T_N of NiO.

6.4. AFM domain pattern observation for 2TO mode excitation (Room temperature to 532 K)

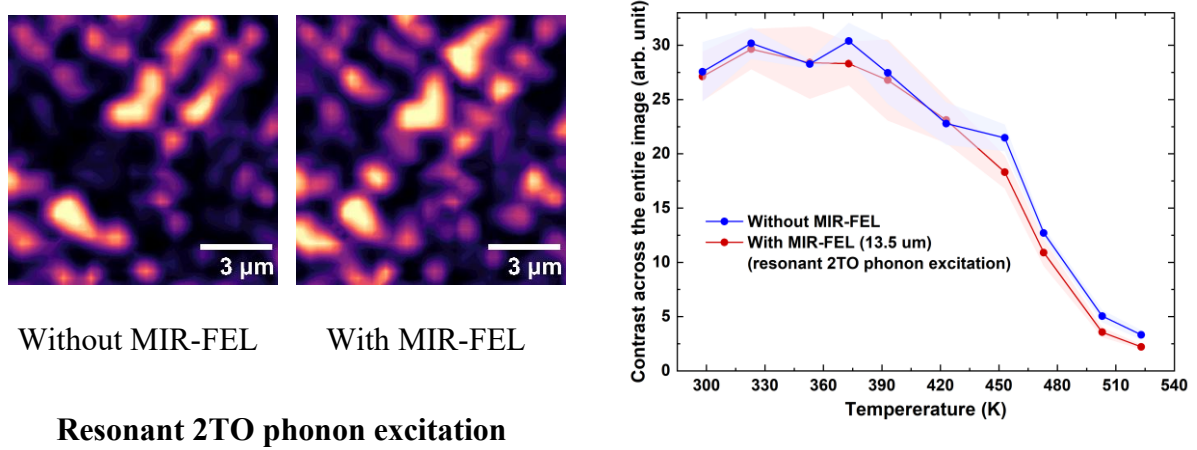
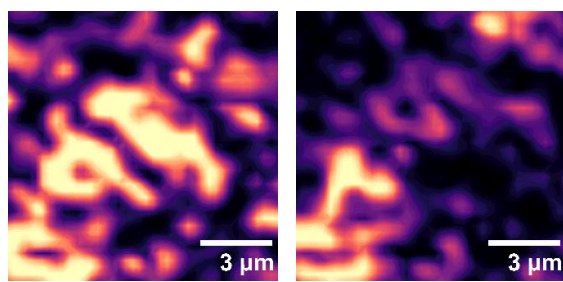


Figure 6.4. (Left) Changes in the AFM domain patterns triggered by resonant 2TO phonon excitation at room temperature. Images of size ($11.19 \times 11.19 \mu\text{m}^2$), (right) Contrast variation across the entire image throughout the temperature cycle for without any external irradiation (blue line and blue shaded standard deviation error band), and with MIR-FEL irradiation at 13.5 μm (red line and red shaded standard deviation error band)

Then, the 2TO phonon mode was resonantly excited by irradiating the sample with MIR-FEL (13.5 μm), while ensuring the relative timing of the MIR-FEL and ns-laser pulses was synchronized. The observation was first conducted at room temperature, which was recorded to be 298 K. The Figure 6.4. on the left presents a close-up image highlighting a portion of the domain pattern changes observed without irradiation and under MIR-FEL irradiation tuned to the 2TO phonon mode wavelength. Then we increased the temperature in 20-30 K steps and recorded images both without and with MIR-FEL irradiation. This process was repeated until the sample temperature reached its T_N and no longer exhibited birefringence. In the Figure 6.4. (right), we show the comparison of contrast variations over the entire observation area of the image ($250 \times 187 \mu\text{m}^2$), where the contrast reduction difference became much more visible after 423 K. This indicates that the MIR-FEL irradiation accelerates the contrast reduction, equivalent to an additional heating of approximately 5 K.

6.5. AFM domain pattern observation for LO mode excitation (Room temperature to 532 K)



Without MIR-FEL

With MIR-FEL

Resonant LO phonon excitation

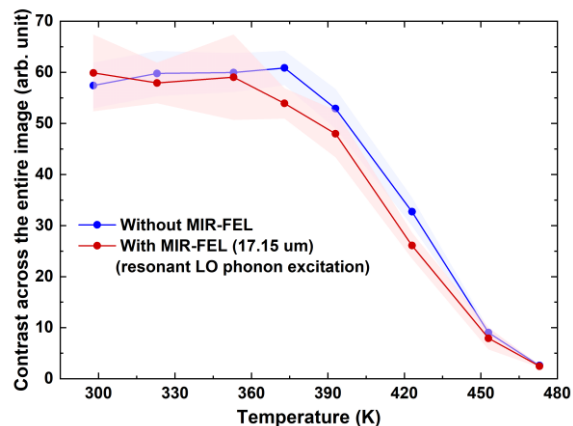


Figure 6.5. (Left) Changes in the AFM domain patterns triggered by resonant LO phonon excitation at room temperature, (right) Contrast variation across the entire image throughout the temperature cycle for without any external irradiation (blue line and blue shaded standard deviation error band), and with MIR-FEL irradiation at 17.15 μm (red line and red shaded standard deviation error band)

Subsequently, the LO phonon mode was resonantly excited by irradiating the sample with MIR-FEL (17.15 μm), with the relative timing of the MIR-FEL and ns-laser pulses coordinated under synchronized conditions. Images were recorded using the same procedures as in the previous experiment. On the left of Figure 6.5. shows a close-up image highlighting a portion of the domain pattern changes observed without irradiation and under MIR-FEL irradiation tuned to the LO phonon mode wavelength, and on the right of Figure 6.5. shows the comparison of contrast variations over the entire observation area of the image. In this case, the contrast reduction rates for conditions without and with MIR-FEL irradiation diverged after ~ 353 K, exhibiting a similar phenomenon of an additional heating equivalent to ~ 5 K.

We then perform a time-resolved pump-probe measurement by varying the relative timing of the ns-laser from overlapping to a delay of up to 5 ms, recording images at each delay. The temperature was carefully maintained at the target level. After completing the observation across all delay stages, the temperature was increased in increments of 20-30 K, and time-resolved measurements were repeated until 523 K was reached.

6.6. Mean Structural Similarity Index Measure (MSSIM)

The Mean Structural Similarity Index (MSSIM)^(21),186,197) extends the original Structural Similarity Index (SSIM)^(185),186) by averaging local SSIM scores across the whole image. While SSIM evaluates similarity between corresponding local patches x and y , MSSIM combines these local measurements across the entire spatial area of the images, yielding a single value that quantifies overall structural similarity relative to the reference image. Taking N small sections of the image, the MSSIM between two images X and Y can be defined as

$$MSSIM(X, Y) = \frac{1}{N} \sum_{j=1}^N SSIM(x_j, y_j) \quad \text{Eq. (6.1)}$$

Because each local SSIM (x_j, y_j) value lies from 0 to 1 and satisfies symmetry and unique maximum at $x_j = y_j$ MSSIM inherits these properties as well. (more details of SSIM analysis on Section 5.6, Chapter 5). Therefore, MSSIM (X, Y) value attains 1 if and only if all corresponding local patches are identical. One limitation to consider regarding SSIM and MSSIM analyses is that they are quite sensitive to spatial shifts, whereby a minor translation of captured images can significantly reduce the SSIM value despite the preservation of pattern similarity remains high.¹⁹⁸⁾ Additionally, this method may underestimate uniform illumination changes across the entire image and color shifts that do not significantly impact the structural content.^{199),200)} The MSSIM is implemented in LabVIEW to analyze all the recorded AFM-domain images from the above measurements.

6.6.1. Results from the MSSIM analysis

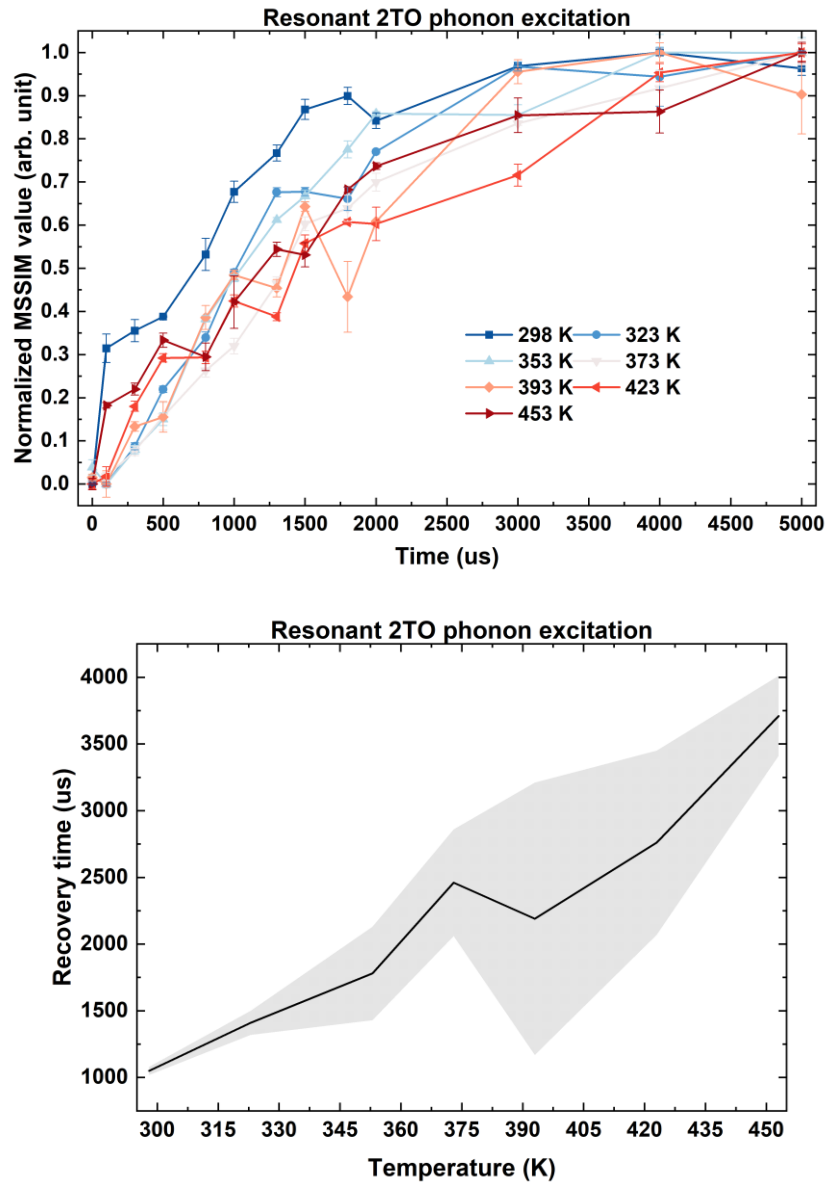


Figure 6.6. (Upper panel) Normalized MSSIM values of images with and without resonant 2TO phonon excitation, (lower panel) Recovery time of the domain pattern similarity, extracted from MSSIM values with respect to temperature.

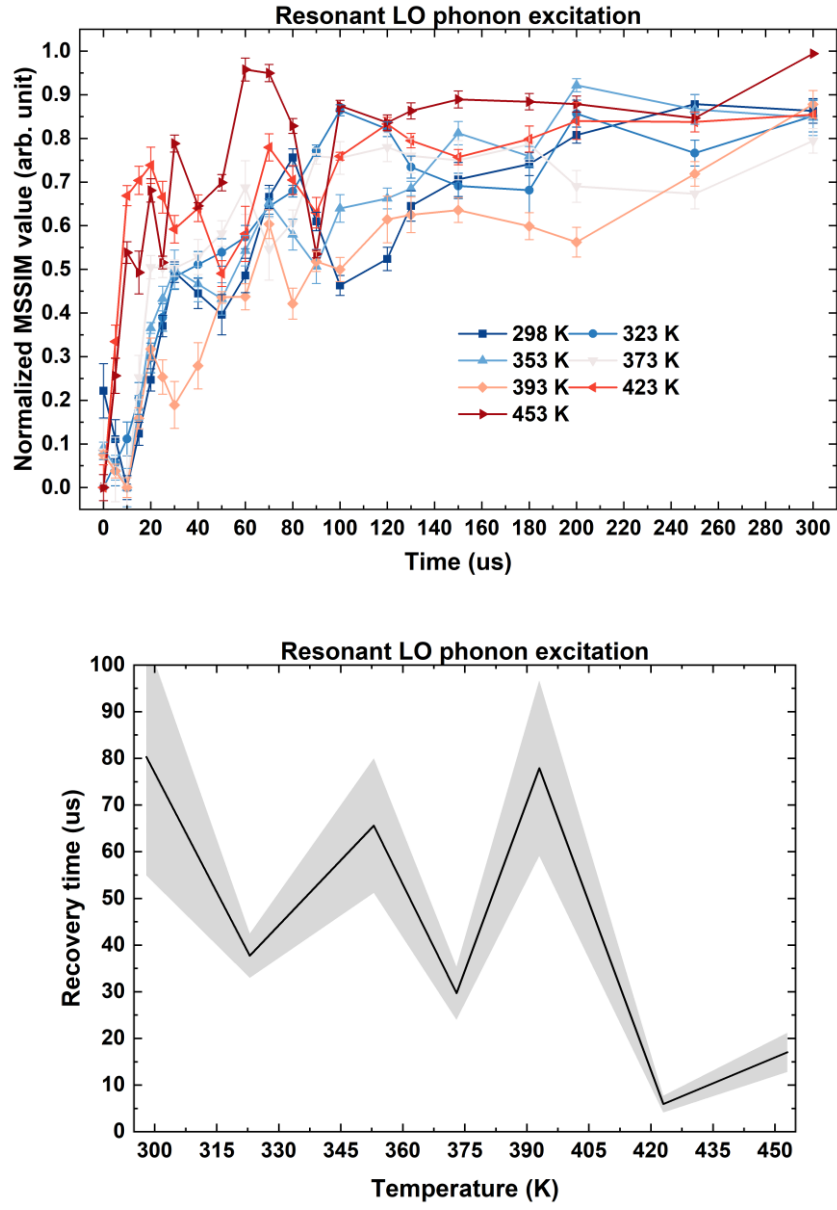


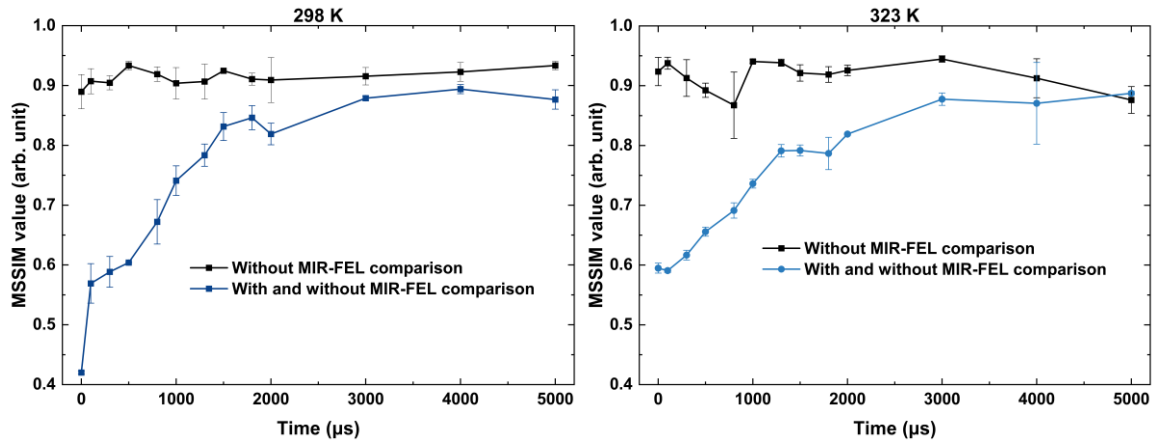
Figure 6.7. (Upper panel) Normalized MSSIM values of images with and without resonant LO phonon excitation, (lower panel) Recovery time of the domain pattern similarity, extracted from MSSIM values with respect to temperature.

For resonant 2TO excitation, the most significant change in AFM domain patterns was observed immediately after MIR-FEL irradiation at room temperature (298 K), followed by an exponential recovery to the original state. (Figure 6.6 (upper panel)) The time constant of the recovery is derived from the exponential decay fitting model

$$y = A_1 \exp\left(-\frac{x}{t_1}\right) + y_0 \quad \text{Eq. (6.2)}$$

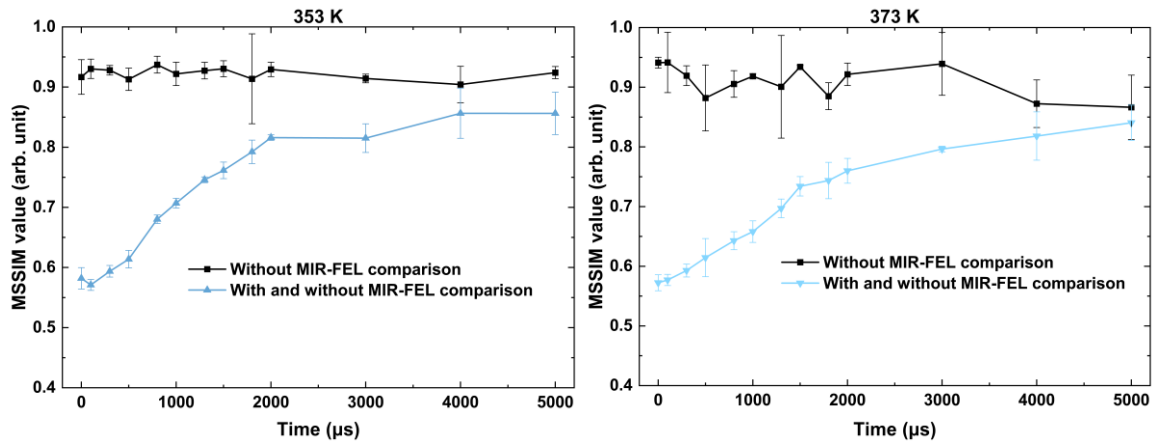
Accordingly, it can be determined that, at 298 K, the 2TO phonon-induced domain modifications recovered with a time constant of 1.05 ± 0.03 ms. As the sample heated, the pattern changes due to excitation persisted longer, and the recovery time progressively increased, reaching 3.7 ± 0.3 ms at 453 K. The normalized MSSIM values and recovery times for resonant 2TO phonon-induced domain pattern changes at all temperatures are illustrated in Figure 6.6. For resonant LO phonon-induced AFM domain pattern changes at room temperature, recovery occurred with a time constant of 80.3 ± 25.4 μ s, approximately one order of magnitude faster than that of 2TO excitation. The recovery time decreased as the temperature increased, with the most rapid recovery recorded at 5.9 ± 1.8 μ s at 423 K. The Figure 6.7 shows the normalized MSSIM values and recovery times for resonant LO phonon-induced domain pattern changes at all temperatures. Images recorded beyond 453 K are not discussed here, because their low contrast yields minimal MSSIM variation.

6.6.2. Confirmation of the thermal impact on domain pattern changes



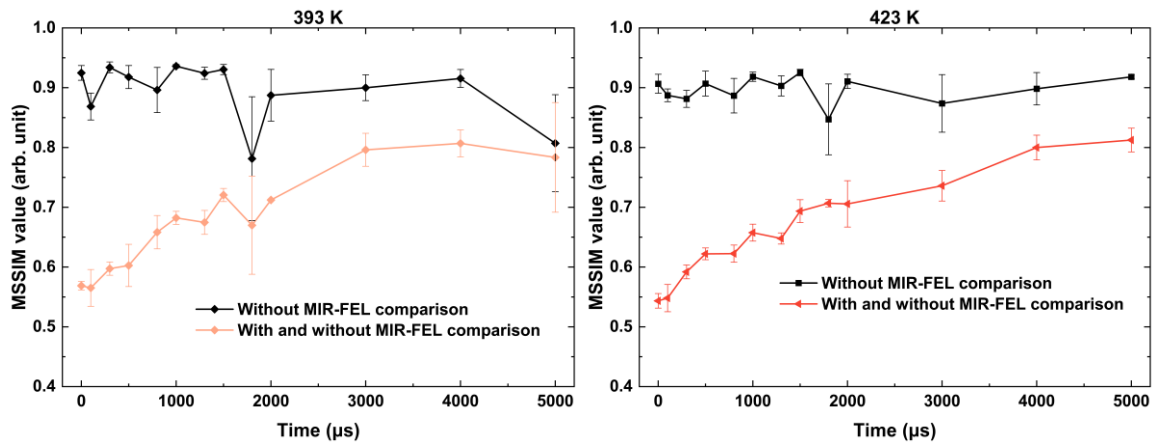
(a)

(b)



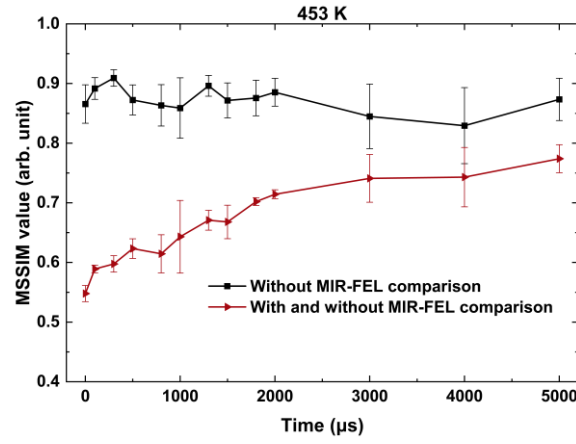
(c)

(d)



(e)

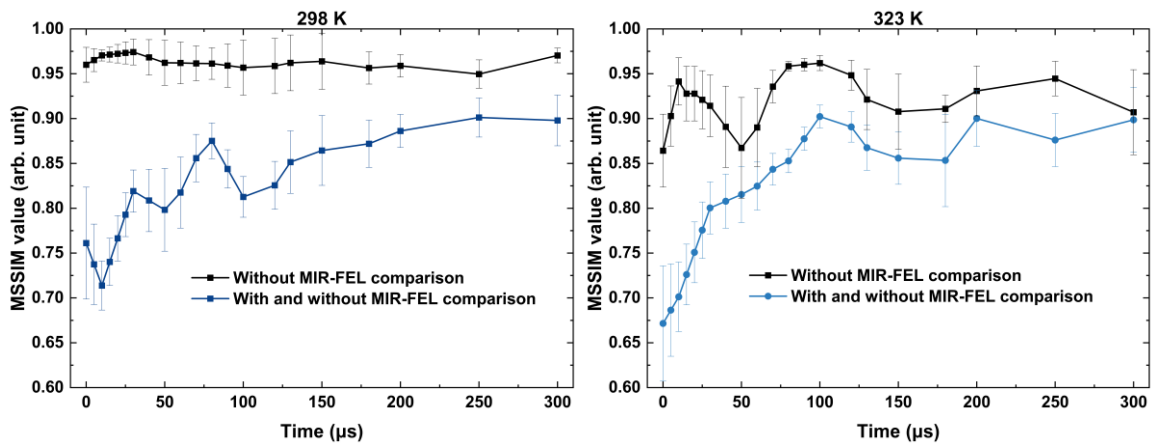
(f)



(g)

Figure 6.8. MSSIM values comparison of AFM domain images with and without 2TO phonon excitation over time at different temperatures

The comparisons of MSSIM values resulting from solely no external irradiation (without MIR-FEL) and with and without MIR-FEL irradiation are also presented. The findings clearly demonstrate that the images recorded without MIR-FEL irradiation exhibit negligible differences, as evidenced by high MSSIM values ~ 0.9 at each probe ns-laser delay stage. Meanwhile, evident fluctuations and recovery rate changes in MSSIM values of with and without MIR-FEL irradiation, indicating that these domain pattern changes are not initiated by thermal effect but rather by resonant excitations. Figure 6.8 (a-g) shows the comparison results for resonant 2TO phonon excitation at different temperatures, up to 5 ms, and Figure 6.9 (a-g) shows the results for resonant LO phonon excitation at different temperatures, up to 300 μs .



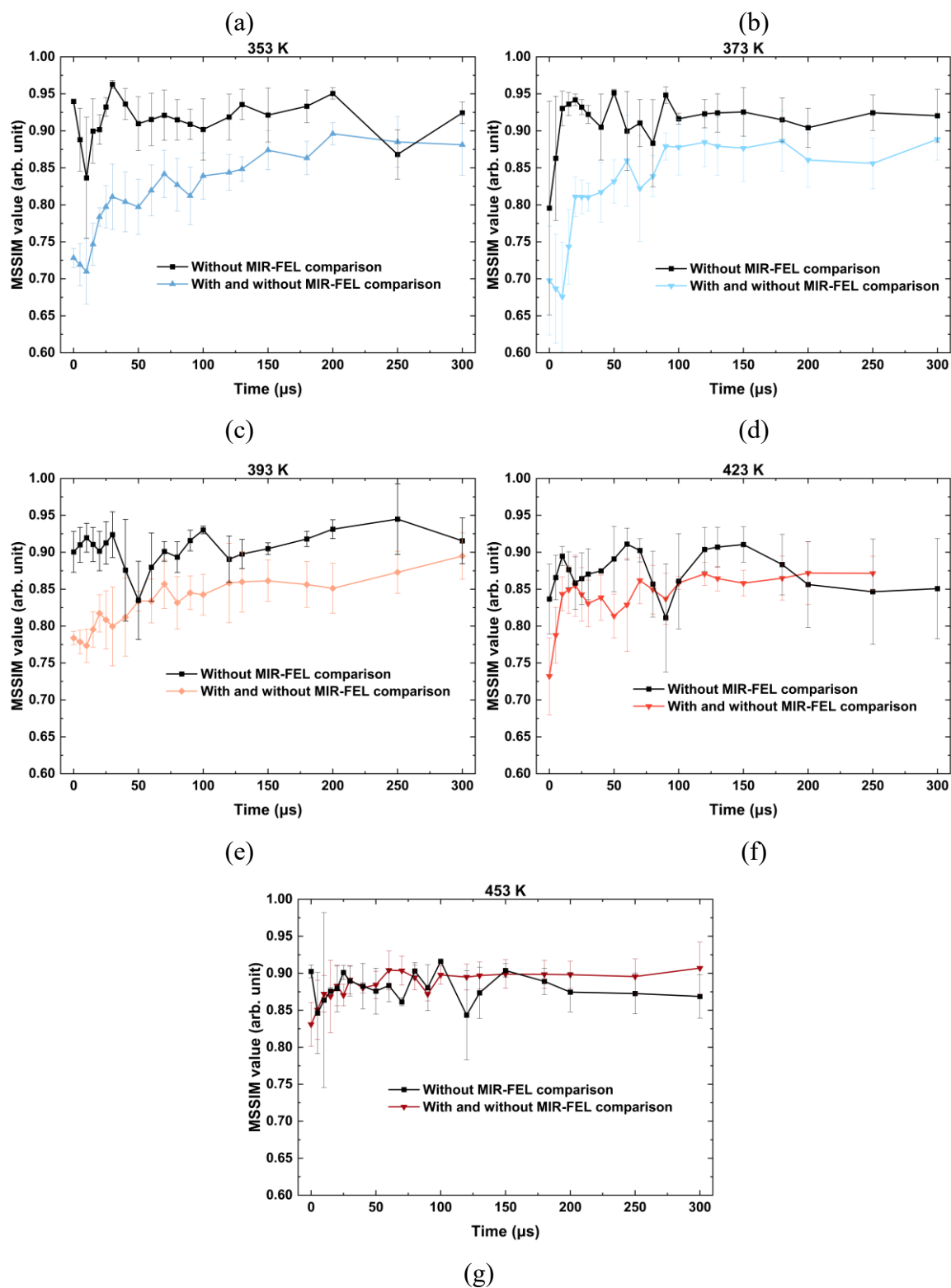


Figure 6.9. MSSIM values comparison of AFM domain images with and without LO phonon excitation over time at different temperatures

If we estimate the phonon lifetimes from conventional linewidth to lifetime conversion ($T=1/(\pi\Gamma)$)^{201),202)}, (T = phonon dephasing time) using Raman linewidths (Γ)^{174),176)}, the intrinsic phonon coherence times are found to lie in the picosecond range, whereas domain recovery dynamics occur in the microseconds to milliseconds timescales. If the recovery process is solely governed by the local interaction of specific phonon and spin, the recovery timescale would be comparable to the phonon lifetime. This phenomenon has been discovered in the study by Sebastian F. Maehrlein et al., where two distinct spin-lattice equilibrations have been observed, one occurring on the picosecond timescale, where recovery is mediated through local spin-phonon energy exchange, and another on the microsecond timescale, where recovery involves collective energy exchange of spins and phonons within the system.²⁰³⁾ Accordingly, our observation of a large difference in phonon lifetimes and magnetic recovery time suggests that even though resonantly excited phonons act as ultrafast perturbations, the domain reconfiguration is governed by much slower processes of spin-lattice relaxations, domain motions with inertia, and collective energy redistributions.^{203)–207)}

Based on first principles ab initio calculations of magnetic switching mediated by phonons in NiO²⁰⁸⁾, it was also stated that elevated temperatures promote enhanced magnetization switching processes. Our experimental results demonstrated that AFM domain changes induced by different resonant excitations display distinct behaviors: one persists for milliseconds and exhibits a slower recovery with increasing temperature, whereas the other recovers within microseconds, and recovery becomes faster at elevated temperatures. These findings are consistent with earlier reports on the contrasting spin-phonon coupling conditions of LO and 2TO phonons,¹⁷⁶⁾ as the magnetic relaxation to the equilibrium state is influenced by the strength and nature of spin-phonon coupling conditions. Positive coupling of spins with the LO phonon mode ($+14.1 \text{ cm}^{-1}$)¹⁷⁶⁾ results in enhanced spin interaction parameters, thereby facilitating more efficient energy exchange as temperature increases. Conversely, negative

coupling of spins with the 2TO phonon mode (-15.7 cm^{-1})¹⁷⁶⁾ counteracts the spin interaction, thereby suppressing energy transitions between spins and phonons and causing a slower relaxation with increasing temperature.

6.7. Conclusion

This chapter demonstrates how specific phonon excitations and thermal conditions distinctly influence AFM domain recovery dynamics. Resonant 2TO and LO phonon excitations were induced via MIR-FEL irradiation, with the sample temperature varied up to the T_N of NiO. Using magneto-optical linear birefringence microscopy, these resonant excitations were observed to trigger ultrafast, transient, and diverse alterations in AFM domains. Domain recoveries following 2TO excitation persist on a millisecond timescale and become prolonged at elevated temperatures, indicating thermally retarded relaxation. In contrast, that of LO excitation occurs within microseconds, and the recovery accelerates with increasing temperature. These observations suggest that phonon-induced AFM domain recovery dynamics are governed by slower, relaxation-dependent collective energy redistribution processes that extend beyond phonon relaxations.

Chapter 6 is mainly adapted from “Ju Yoon Hnin Bo et al, “Resonant phonon-induced magnetic domain dynamics as Néel temperature is approached in nickel oxide”, 2026 *Jpn. J. Appl. Phys.* **65** 023001. , DOI: 10.35848/1347-4065/ae3410”.

Chapter 7

Conclusion and Future Perspectives

7.1. Summary and conclusion

This thesis discussed how intense MIR-FEL pulses from KU-FEL can be harnessed to selectively excite specific phonon modes, with the goal of demonstrating and understanding phonon-assisted energy transfers in strongly correlated systems.

Chapter 1 outlined the motivation for achieving energy-efficient, rapid control of material properties, where phononic control appeals as a promising pathway, particularly in strongly correlated materials, and why two representatives of strongly correlated materials, SrTiO₃ and NiO, were examined.

Chapter 2 presented the fundamental concepts of phonons and spins, and their interactions in strongly correlated systems, thereby providing the theoretical basis for phonon-assisted energy transitions in the subsequent chapters.

In Chapter 3, precise pump-probe laser timing control of the MIR-FEL and a ps-laser was achieved by exploiting sum-frequency generation from a nonlinear ZnS Cleartran® crystal. Sum-frequency generation signal peaks are observed when the two lasers are synchronized. Unforeseen high-order SFG spectra have also been observed simultaneously with the conventional SFG spectrum.

In Chapter 4, specific phonon-assisted electron-phonon energy transfer in SrTiO₃ was demonstrated. Selective excitation of the first-order Raman-forbidden LO₃ phonon mode was achieved via MIR-FEL irradiation. Since conventional Raman spectroscopy cannot access this due to symmetry constraints, the selectively excited phonon-assisted light scattering was

confirmed using anti-Stokes hyper-Raman scattering spectroscopy in a pump-probe experimental configuration. These results establish hyper-Raman scattering as a crucial diagnostic pathway for phononic control in centrosymmetric perovskites.

In Chapter 5, specific phonon-assisted spin-phonon energy transfer in NiO was demonstrated by observing the antiferromagnetic domain dynamics using time-resolved magneto-optical birefringence microscopy. Without external excitation, the domain patterns are static, and with resonant MIR-FEL pumping of the 2TO phonon mode, they are displaced instantly. Using the structural similarity index measure image analysis, a slow exponential recovery of the domain pattern reconfiguration on the millisecond timescale has been observed.

In Chapter 6, it was demonstrated that different phonon modes induced different AFM order reconfigurations through distinct spin-phonon couplings in NiO. The comparison of LO and 2TO phonon-driven domain dynamics was performed at different temperatures (from Room temperature to the Néel temperature of NiO). From the analysis results using the mean structural similarity index measure matrix, it was revealed that excitation of the LO phonon mode yielded much faster microsecond-scale domain recovery. Additionally, the LO mode-driven recovery accelerates with heating, whereas the 2TO mode-driven recovery slows down with temperature. The temperature-resolved measurements confirm that the observed dynamics are governed by intrinsic spin-phonon interactions rather than external heating. These results are consistent with first-principles predictions, where opposite spin-phonon coupling conditions are found for LO and 2TO phonons.

In conclusion, this study demonstrated how tailored laser systems can reveal specific phonon-assisted energy transitions, thereby showing changes in material properties in real time.

7.2. Future Perspectives

This study is one of many steps toward a deeper understanding of the interconnections among specific phonon modes and other quasiparticles, and of their influence on the macroscopic properties of materials. Looking ahead, as the ability to access, drive, and monitor target phonons continues to expand with advancing MIR-FEL technology, it becomes increasingly realistic to envision nonlinear phononic control as a foundation for ultrafast, low-power functional devices. Future research that extends the temporal and spatial resolution of current techniques will probably reveal more complex dynamics, including non-equilibrium phases and hidden parameters that emerge only under resonant vibrational driving. From a materials perspective, expanding experiments from bulk materials to thin films, multilayers, and heterostructures could significantly improve their technological relevance, paving the way for phonon-driven control in real-world devices. From the imaging and image analysis framework, developing automated tracking that can overcome image movements caused by thermal expansion during measurement, along with machine-learning-assisted classification of domain patterns, would enable high-quality and quantitative mapping of domain dynamics over a broader range of parameters. This approach would also generate valuable training data for data-driven models that predict domain responses across various phonon-drive protocols. Ultimately, if compact mid-IR or THz sources can replicate key features of such MIR-FEL-based control, the concepts demonstrated in this work could be transferred from large-scale facilities to tabletop platforms, making phonon-engineered manipulations more accessible.

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Achievements

Peer-reviewed publications

- [1] Bo, J.Y.H., Zen, H., Yoshida, K. et al. Observation of Selective Excitation of Raman Inactive Phonon Mode of Strontium Titanate Through Anti-Stokes Hyper-Raman Scattering Process. *J Infrared Milli Terahz Waves* **45**, 999–1009 (2024).
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- [2] Ju Yoon Hnin Bo et al, “Measurement of temporal evolution of antiferromagnetic domain change in nickel oxide driven by 2TO phonon mode excitation via pump-probe experiment”, 2024 *Jpn. J. Appl. Phys.* **63** 112001
DOI: 10.35848/1347-4065/ad879c
- [3] Ju Yoon Hnin Bo et al, “Resonant Phonon-Induced Magnetic Domain Dynamics as Neel Temperature is Approached in Nickel Oxide”, 2026 *Jpn. J. Appl. Phys.* **65** 023001
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International conference proceedings

- [1] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, "Mode-Selective Phonon Excitation of SrTiO₃ by MIR-FEL with Anti-Stokes Hyper-Raman Scattering Spectroscopy," *2021 46th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz)*, Chengdu, China, 2021, pp. 1-2, doi: 10.1109/IRMMW-THz50926.2021.9567366.
- [2] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, "Selective excitation of LO₃ phonon mode of SrTiO₃," *2022 47th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz)*, Delft, Netherlands, 2022, pp. 1-2, doi: 10.1109/IRMMW-THz50927.2022.9895839.

- [3] Ju Yoon Hnin Bo et al, “Observation of high order sum frequency generations observed in polycrystalline ZnS,” 41st International Free Electron Laser Conference (FEL2024), Submitted.

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- [2] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, “Anti-Stokes Hyper-Raman Scattering Spectroscopy of Strontium Titanate for Mode-Selective Phonon Excitation Using Mid-Infrared Free Electron Laser,” 30th Japan Infrared Society Research Presentation Program (Virtual), Poster
- [3] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, “Selective excitation of LO₃ phonon mode of SrTiO₃,” 47th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz 2022), Delft, Netherlands, Poster
- [4] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, “Observation of Multi-photon Sum Frequency Generation in ZnS Crystal,” 13th International Symposium of IAE, Kyoto, Japan, Poster
- [5] J. Y. H. Bo, H. Zen, R. Akasegawa, K. Hachiya, K. Yoshida and H. Ohgaki, “Hyper-Raman Scattering Spectroscopy of the Selective Phonon Excitation of Strontium Titanate Using Mid-Infrared Free Electron Laser,” 28th FEL and High-Power Radiation Study Group Workshop, Japan (Virtual), Oral
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- [10] Ju Yoon Hnin Bo, Heishun Zen, Hideaki Ohgaki, “Measurement of the temporal evolution of antiferromagnetic domain switching in nickel oxide driven by 2TO phonon mode excitation via pump-probe experiment,” 5th International Congress on Advanced Materials Sciences and Engineering 2024 (AMSE 2024), Lovran, Croatia, Oral
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- [13] Ju Yoon Hnin Bo, Heishun Zen, Hideaki Ohgaki, “Kyoto University Free Electron Laser Facility (KU-FEL) (Current and Ongoing Developments),” 49th International Conference

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