

Nonlinear phononics in rare-earth orthoferrites

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Harnessing nonlinear interactions between phonon modes in condensed matter presents a powerful avenue for tailoring material properties for innovative applications in future information devices. Here we report a study of nonlinear coupling between infrared (IR) active and Raman-active phonon modes in rare-earth orthoferrites ErFeO_3 , TmFeO_3 , and TbFeO_3 . To reveal the nonlinear phonon interactions, we resonantly excite IR-active phonons with an ultrashort midinfrared pulse, with its central wavelength tunable in the 3–18 μm (16.5–100 THz) range, and trace the phonon modes in the time domain after the excitation. We identify two main coupling mechanisms: quadratic linear and trilinear, which stand for a nonlinear coupling of the Raman-active phonon with either one or two distinct IR-active modes, respectively. The origin of driving each Raman-active phonon mode is identified and analyzed with polarization-dependent pump-probe spectroscopy. Our results show a strong dependence of the trilinear coupling mechanism on the crystallographic orientation of the sample, thus revealing that only specific phonon modes can exhibit this coupling.

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I. INTRODUCTION

Emerging technologies call for faster and more efficient means of controlling material properties, such as electric conductivity, magnetic order, and refractive index. One stimulus can modify all these parameters together—lattice distortion. A conventional way to produce such a distortion at GHz and even THz frequencies is by employing picosecond ultrasonics [1,2]. In this way, a transducer is required for the generation of a strain pulse, usually a material with a large thermoelastic coefficient. Despite their simplicity and efficiency, such transducers have significant drawbacks: the absorbed energy of the laser pulse in a photoexcited thermoelastic material leads to unavoidable heating and stretching of the generated strain pulses due to the high relaxation time [3]. Instead, applying a resonant phonon excitation via infrared (IR) laser sources grants a powerful tool for a nonthermal coherent control of lattice-mediated (phonon-mediated) phenomena [4].

Low-energy midinfrared (MIR) laser sources offer direct access to multiple phonon modes in solids. A conventional tabletop MIR laser-based generator provides fine tuneability in a 16.5–100 THz (3–18 μm) spectral range, subpicosecond resolution, and extreme electric field reaching a few tens of MV/cm. These parameters are of great interest for the modern studies of ultrafast dynamics in materials. In particular,

such pulses allow photon energy to be transferred right to the lattice, avoiding electronic transitions. In this way, numerous experiments on nonlinear phonon interactions—“nonlinear phononics”—have recently demonstrated an effective control of material properties via resonantly excited IR-active phonons. In the pioneering works exploiting the coherent excitation of the IR-active phonon modes, an ultrafast electronic phase transition in manganite after the resonant excitation of the Mn-O stretching mode [5,6] was reported. Fascinatingly, resonant excitation of the Cu-O vibration modes was found to be responsible for a transient enhancement of superconductive transport in cuprates [7,8]. An efficient coherent magnetization switching has been recently predicted in the insulating yttrium iron garnet via resonantly excited IR-active phonons [9].

The recent progress in generating chiral optical phonons and their application to control magnetically ordered materials is even more exciting [10]. It has been predicted theoretically that the circular motion of the ions, carrying orbital magnetic moments, may induce an effective magnetic field reaching a few tens of tesla [11–13]. Experimentally, a manifestation of this significant effective magnetic field, mediated by excitation of the chiral phonons, has so far been reported in materials lacking magnetic order: CeF_3 , SrTiO_3 , and Al_2O_3 [14–16].

The phonon-induced lattice distortion leading to modification of the exchange interaction was found to be a powerful mechanism to control the magnetic order in rare-earth substituted orthoferrites and garnets [17,18]. When using spectrally broad MIR pulses (bandwidth $\Delta\nu \sim 4$ THz), in specific geometries, simultaneous excitation of two orthogonal phonon modes can be achieved, leading to an elliptical ion motion [19]. Accordingly, as the phonon chirality defines the polarity

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of an effective magnetic field, a similar effect can be achieved with a simultaneous excitation of two distinct linear phonon modes with a phase shift between them. Thus, coherent MIR sources with their abilities for selective phonon excitation [20] and directional control of the effective field grant a robust manipulation tool for the lattice-mediated phenomenon. Understanding the phonon interactions in archetypal materials is the key incentive in the new field of nonlinear phononics.

While MIR excitation drives only IR-active phonons, observing related Raman-active phonons can indicate nonlinear phononic coupling. The excitation occurs via the mechanism of impulsive stimulated Raman scattering, which is enhanced by the resonant pumping of IR-active phonons [4], the phenomenon called ionic Raman scattering. In the presence of nonlinear interaction between Raman-active and IR-active phonons, the reduced potential energy of the lowest-order interacting modes can be written as [20]

$$V(\mathbf{Q}) = c_{iR} |Q_{iR}|^2 Q_R + c_{jR} |Q_{jR}|^2 Q_R + c_{ijR} Q_{iR}^* Q_{jR} Q_R + c_{ijR} Q_{iR} Q_{jR}^* Q_R. \quad (1)$$

Here, the Q_{iR} and Q_R denote the normal coordinates of IR and Raman modes, respectively; the subscripts 1, 2, and 3 represent different symmetries; c_{iR} are cubic anharmonicity coefficients. The first two quadratic-linear terms in the potential energy are responsible for the nonlinear coupling of a single IR-active mode to a symmetric Raman-active mode. While the resonantly excited IR mode comprises ionic oscillations near their equilibrium positions, a nonlinear coupling provides a force exerted on the Raman mode, which follows the envelope of these oscillations. Due to the quadratic behavior, the direction of the driving force is independent of the phase of the IR-active mode. An alternative mechanism to anharmonic lattice coupling was recently proposed and referred to as infrared-resonant Raman scattering [21]. The mechanism is based on the simultaneous excitation of IR- and Raman-active modes and, in certain materials, entails an order-of-magnitude enhancement in the signal relative to the quadratic-linear coupling. However, in our measurements, these two effects cannot be distinguished, and no enhancement was observed. The last two terms in the potential energy [Eq. (1)] describe an utterly different trilinear coupling mechanism between two orthogonal IR-active modes of distinct symmetries and a single Raman-active phonon mode. Comparing the two distinct coupling terms above, the trilinear coupling regime is more attractive for application because of its unique symmetry properties that allow for changing the direction of an effective driving force. Since this coupling involves two orthogonal IR-active modes, the direction of the effective force acting on the Raman-active phonon mode depends on the mutual phase between the two IR-active modes. Thus, the π phase shift between two coupled IR-active modes will alter the direction of the effective force reflected by the π shift of the Raman phonon phase. This mechanism allows for controlling the direction of the lattice distortion (effective force) through the polarization of the driving MIR pulse. The coupling mechanism between the IR- and Raman-active phonons can be retrieved from the phase and amplitude analysis of the excited phonon dynamics as a function of the pump polarization.

In this work, we experimentally investigate mechanisms of nonlinear phonon coupling in rare-earth orthoferrites ($R\text{FeO}_3$), a unique family of magnetic oxides serving as a platform to explore a variety of phenomena such as ultrafast magnetism, spin reorientation phase transitions, and quantum cooperativity [22]. Here, we experimentally demonstrate how quadratic-linear ($|Q_{iR}|^2 Q_R$) or trilinear ($Q_{iR}^* Q_{jR} Q_R$) interactions can be distinguished, and how the various crystallographic orientations and the rare-earth composition affect the nonlinear phonon coupling. We apply the polarization-dependent pump-probe technique to differentiate the nonlinear coupling mechanisms and the involved phonon modes.

II. MATERIALS AND METHODS

A rare-earth orthoferrite, $R\text{FeO}_3$, is a distorted perovskite with a unit cell containing 20 atoms. A theoretical analysis of the $Pbnm$ space group predicts 60 phonon modes at the center of the Brillouin zone [23,24]: $7A_g$, $17B_{(1,2,3)g}$, $8A_u$, and $28B_{(1,2,3)u}$. Among them, the A_g and B_{ig} are Raman-active modes. Since the material has a centrosymmetric crystal structure, the IR and Raman activities are mutually exclusive. The low-energy Raman modes ($\nu < 8$ THz) are those involving heavy atom displacement, i.e., $R\text{-O}$ bond stretching, therefore their frequencies vary slightly for different rare-earth elements. Only B_{1u} , B_{2u} , and B_{3u} are polar modes with electric dipole moments. Therefore, they are sensitive to an external electric field and can be resonantly excited by MIR light, polarized along their dipolar moment. Due to the instrumental limitations, only high-frequency polar modes (> 15 THz) can be accessible with a conventional MIR laser source. For the rare-earth orthoferrites family, only three polar phonon modes lie above 15 THz (below 20 μm) [25–27], i.e., $B_{3u}(9)$, $B_{2u}(9)$, and $B_{1u}(7)$ with frequencies close to 16.6, 15.8, and 16.2 THz, respectively (the number in brackets indicates the order of the phonon mode and will be skipped in further reference). They correspond to Fe-O bonds stretching along distinct crystallographic directions [28], and therefore require a particular pump polarization for the excitation, along a , b , and c crystallographic directions, respectively [see inset in Fig. 1(a)]. Due to the optical phonon Reststrahlen bands, the absorption and reflection coefficients increase drastically in this spectral region [29]. The absorption coefficients for high-frequency B_{1u} , B_{2u} , and B_{3u} modes were calculated using the IR absorption data from Refs. [24,26], and yield 2400, 1950, and 2000 cm^{-1} , respectively.

In $R\text{FeO}_3$, the only symmetry allowed for nonlinear couplings between combinations of phonon modes is that containing the A_g representation. In Eq. (1), the quadratic-linear ($B_{iu}^2 A_g$) term corresponds to a coupling between a single IR-active mode (B_{iu}) and a symmetric A_g Raman-active mode. The amplitude dependence of the A_g mode on the pump polarization can reveal the IR-active B_{iu} mode with which it is coupled. In turn, the trilinear coupling term ($B_{iu}^* B_{ju} B_{kg}$) with $i, j, k = 1, 2, 3$ ($i \neq j \neq k$) corresponds to an interaction between two orthogonal IR-active modes (B_{iu} and B_{ju}) and an antisymmetric Raman-active mode B_{kg} . As discussed earlier, if the coupling is trilinear, then not only the B_{kg} phonon amplitude but also its phase will be dependent on the incident pump

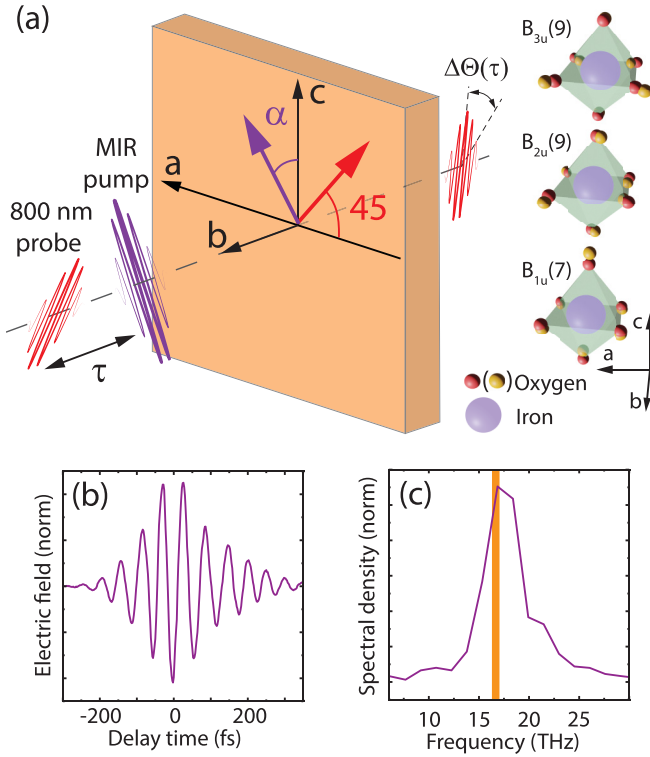


FIG. 1. (a) A schematic of the experimental pump-probe geometry: A linearly polarized MIR pulse with a variable polarization angle α is absorbed by high-frequency IR-active phonons, which are represented by Fe-O bonds stretching along different crystallographic directions (inset); the induced lattice dynamics is traced through the time evolution of the probe pulse polarization. (b) A time trace of the 250 fs MIR pump pulse, measured via the electro-optical sampling (EOS) technique in an exfoliated GaSe film gated by a 10 fs pulse generated in a home-built noncollinear parametric amplifier. (c) The Fourier transformation of the EOS signal is presented in Fig. 1(b). A spectral region containing the high-frequency IR-active phonon modes is highlighted in orange.

polarization, showing a π shift upon reversal of the polarity of one of the IR-active phonons.

All samples used in our measurements are single-crystal orthoferrites grown by the floating zone technique with radiation heating [30], which include TbFeO₃ (a - and b -cuts), TmFeO₃ (a -cut), and ErFeO₃ (b -cut). All samples were ≈ 60 μm -thick plates polished to an optical-grade surface.

Excitation of Raman-active phonons mediated by MIR-driven IR phonons was examined at room temperature using a time-resolved pump-probe technique. The amplified laser system, delivering 800 nm pulses at a 1 kHz repetition rate, was used for pumping the double optical parametric amplifier (OPA) (see Fig. 4 in the Appendix). The tunable MIR pump pulse was generated by mixing two pulses from two slightly detuned OPAs in a noncollinear differential frequency generator. The pump wavelength was tuned to resonate with the highest IR-active phonon modes located around 18 THz. The spectra-temporal properties of the MIR pump were measured using an electro-optical sampling (EOS) [Fig. 1(b)]. The extracted pump pulse duration was approximately 250 fs at full width at half maximum. The Fourier spectrum of

the measured EOS signal is depicted in Fig. 1(c) with a shaded orange region indicating the highest-frequency IR-active phonon modes. The large spectral width of the pump pulse of ≈ 4 THz renders the difference between the frequencies of the IR phonons B_{3u} , B_{2u} , and B_{1u} negligible in the samples with different crystallographic directions and compositions. A set of three parabolic mirrors was used in a $4f$ geometry to efficiently focus the pump beam into a 50 μm spot, with a fluence reaching up to ≈ 100 mJ/cm^2 . A small part of the time-delayed 800 nm fundamental beam was focused ($d \approx 15$ μm) on the sample in the collinear geometry and used as a probe. The associated penetration depth of the pump is only ≈ 5 μm , which is much smaller than the sample thickness. Therefore, the polarization state of the probe is affected only in a thin region of the sample; thereafter the probe propagates through the unexcited region of the sample. The detected phonon modes are nonpropagating within the photoexcited region of ≈ 5 μm , rendering propagation effects negligible. Instead of conventional detection techniques, such as transient reflectivity or transmission measurements [31,32], used for Raman phonon detection, in this work, we use polarization detection [19,33,34] due to the higher signal-to-noise ratio. If excited, the coherent Raman-active phonon modulates the dielectric tensor of RFeO₃ according to the symmetry of the corresponding Raman tensors [26], and thus can be observed in the oscillations of the crystallographic linear dichroism [33,35]. Owing to the strong birefringence in orthoferrites, which distorts the conventional detection selection rules for the Raman-active phonons, phonons of the both A_g and B_{kg} symmetries can be detected by probe pulses polarized at 45° to the crystallographic axes. To retrieve the properties of Raman-active modes, a transient variation of the probe polarization rotation as a function of the pump-probe delay was registered using balanced detectors and a lock-in technique [19], and then analyzed in the time and frequency domains.

The experimental geometry is sketched in Fig. 1(a): Pump and probe beams arrive at normal incidence. The probe polarization was fixed at 45° with respect to the in-plane crystallographic axes, enabling simultaneous detection of the orthogonal Raman-active modes. To identify the coupling mechanism, the angular dependence of the phonon amplitude and the phase as a function of the pump polarization ($\alpha = 0^\circ, 45^\circ, 90^\circ, 135^\circ$, and 315°) were analyzed [36]. To identify the relative phase of the Raman-active phonons, we applied numerical spectral filtering to isolate a single phonon mode in the time domain. The filtering process consists of the following steps: calculating the complex Fourier transform, isolating the desired phonon mode by applying the bandpass filtering to the spectral data (with cutoff frequencies chosen at the minima in the spectral density below and above the phonon band), and performing the inverse Fourier transform.

III. EXPERIMENTAL RESULTS

The indicative probe polarization dynamics in the b -cut TbFeO₃ are depicted in Fig. 2. The raw data for the transient probe polarization rotation for the pump ($\nu_{\text{pump}} \approx 18$ THz) polarized at $\alpha = 45^\circ$ with respect to the c axis are shown

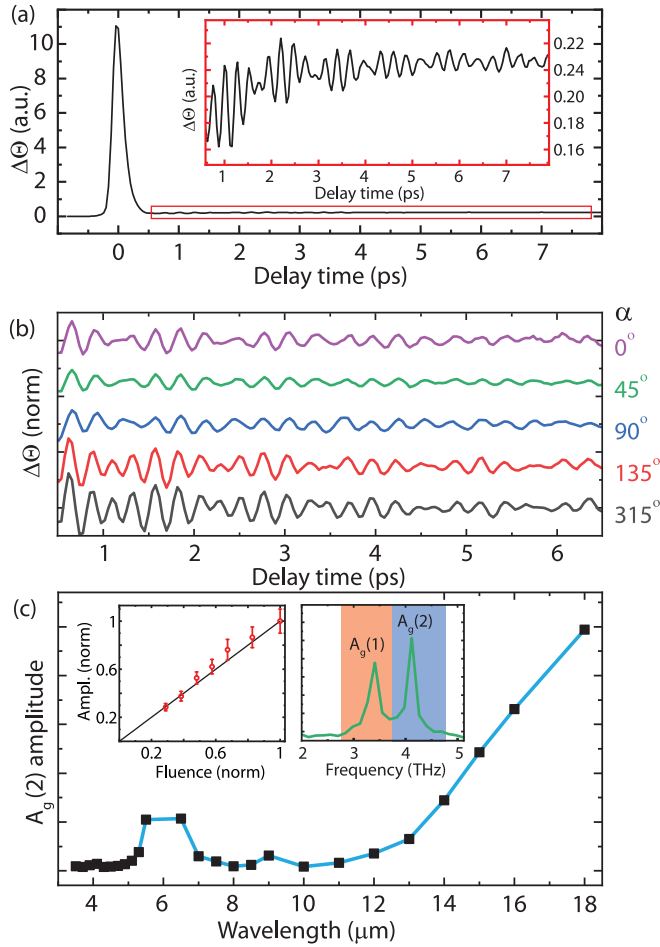


FIG. 2. (a) The indicative transient polarization rotation measured in the *b*-cut TbFeO₃: At $\tau = 0$ ps, the strong change in polarization is due to the optical Kerr effect driven by the pump electric field directly, followed by the lattice relaxation (at $\tau > 0.5$ ps) and coherent oscillations with a beating behavior (inset). (b) The extracted phonon dynamics for different angles of the pump polarization, with the pump wavelength fixed at 18 μm (16.5 THz). (c) The normalized amplitude of the symmetric Raman-active $A_g(2)$ mode as a function of the pump wavelength in TbFeO₃. The two insets show its fluence dependence (red circles) with a linear fit (black line) and an indicative Fourier spectrum with the two A_g phonons.

in Fig. 2(a). The dynamical signal is dominated by the peak response at $\tau = 0$ followed by the long-lived oscillations [see inset in Fig. 2(a)]. For further analysis of the pump-induced dynamics, only the oscillating tail starting from $\tau \approx 0.5$ ps was considered. The double-exponential offset observed in the inset of Fig. 2(a), with characteristic times of ≈ 8 and ≈ 100 ps, ascribed to the phonon thermalization and cooling down of the sample, respectively, was removed to facilitate the analysis of the oscillatory dynamics. Figure 2(b) shows the extracted probe polarization dynamics for the five different pump polarizations. A frequency beating in the time traces, observed for all pump polarizations, indicates the presence of a few simultaneously excited modes with closely lying frequencies [37,38]. Indeed, the Fourier transformation of the dynamical signal reveals the existence of two oscillation modes with corresponding frequencies of 3.4 and 4.2 THz [see inset in

Fig. 2(c)]. Regarding the values of these frequencies, they both can be attributed either to symmetric A_g or antisymmetric B_{1g} Raman-active phonon modes [26] since they have similar frequencies. A proper distinction between the modes can only be made by analyzing the isolated mode's pump polarization dependence and frequency. Figure 2(c) shows the amplitude of the phonon mode at 4.2 THz normalized with respect to the incident pump fluence in the *b*-cut TbFeO₃ sample as a function of the pump wavelength. Above 10 μm , a drastic increase in the phonon amplitude was observed, indicating resonant conditions for the IR phonon excitation. The amplitude of the Raman-active phonons shows a linear dependence on the fluence of the pump, the frequency of which is tuned in resonance with IR-active phonons [inset in Fig. 2(c)]. All of this confirms the nonlinear phononics scenario. A minor enhancement of the phonon amplitude was also observed at $\approx 6\text{-}\mu\text{m}$ pump wavelength [Fig. 2(c)], where the electronic transition ($^7F_6 \rightarrow ^7F_5$) of Tb³⁺ ions takes place [29]. A similar effect was recently reported in the dysprosium orthoferrite (DyFeO₃), where a resonantly excited *f-f* transition of the Dy³⁺ ions was responsible for the THz lattice dynamics [39]. This effect is omitted from the discussion below, and we focus on the dynamics excited by the pump pulse with the central frequency of 18 THz.

The indicative phonon dynamics for all studied samples are depicted in Fig. 3(a) as excited by the pump with the same polarization $\alpha = 45^\circ$. In all samples, signatures of several excited phonon modes are seen in the obtained signals. The difference in signal amplitude observed across different rare-earth compositions and crystallographic orientations is likely defined by the detection conditions, i.e., the effect of the phonon-induced linear dichroism along specific crystallographic directions. A close look at the Fourier spectra of the temporal signals in the *b*-cut ErFeO₃ at different polarizations of the pump [see Fig. 2(b)] reveals a distinct behavior of two coexisting Raman-active modes centered at 3.4 and 4.2 THz. Unlike the first Raman mode, for which the amplitude shows nearly isotropic behavior, the second mode has a clear minimum when the pump polarization is aligned along the *a* axis ($\alpha = 90^\circ$), indicating a weak quadratic-linear coupling between the Raman and the IR-active B_{3u} phonons.

At the intermediate pump polarizations ($\alpha = 45^\circ$, 135° , and 225°), the electric field of the pump pulse has projections on both crystallographic axes lying in the sample plane, and both IR-active modes (B_{1u} and B_{3u}) can be excited simultaneously. Both interaction mechanisms (quadratic linear and trilinear) can take place. To distinguish them, we performed a phase analysis of a chosen Raman-active phonon mode as a function of the incident pump polarization. After applying high-pass or low-pass filters to the data, the corresponding Fourier spectra were back-transformed to the time domain. Thus, each Raman-active phonon mode can be analyzed independently. In Fig. 3(c), we compare two phonon modes for two orthogonal pump polarizations ($\alpha = 45^\circ$ and 135°). The electric field projection on the *a* axis has the same amplitude and phase for those two polarizations, thus preserving the phase of the excited B_{3u} phonon. However, the projection on the *c* axis has identical amplitude but opposite phases, resulting in a flipped IR-active B_{1u} phonon phase. The fact that phonon dynamics shows identical phases in both

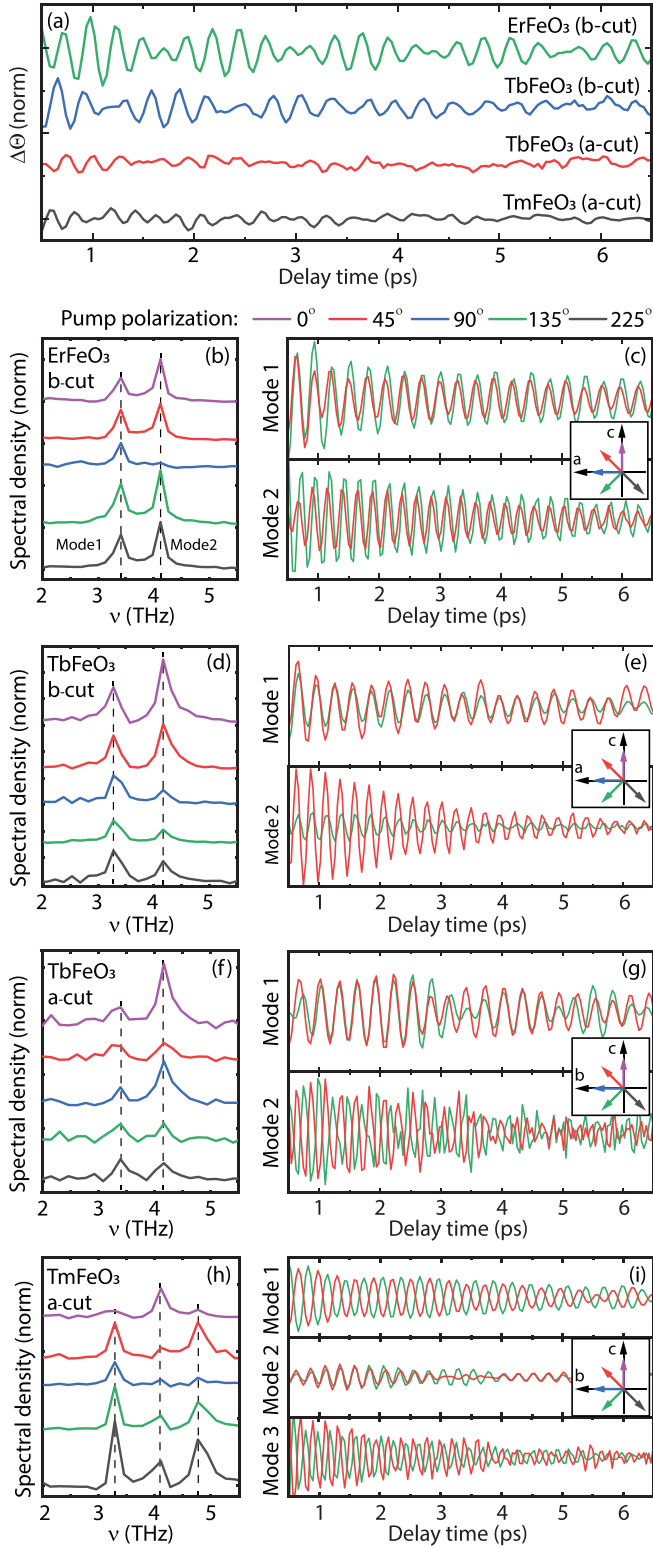


FIG. 3. (a) Indicative Raman phonon dynamics for different RFeO₃, obtained with the same pump polarization ($\alpha = 45^\circ$). (b), (d), (f), (h) Fourier transformations of the time domain signal for a series of pump polarization angles ($\alpha = 0^\circ, 45^\circ, 90^\circ, 135^\circ$, and 225° ; see inset) for an indicated sample. (c), (e), (g), (i) Comparison of time domain signals of isolated phonon modes for two orthogonal pump polarizations ($\alpha = 45^\circ$ and 135°) on each graph. The inset shows the color-coded pump polarization angles.

configurations implies that the quadratic-linear ($B_{iu}^2 A_g$) coupling regime is responsible for the excitation. We note the small phase shift in the case of mode 2 originating from a possible pump-probe overlap drift. The pump polarization analysis concludes that both frequencies are related to the symmetric $A_g(1)$ and $A_g(2)$ phonon modes. However, the fact that the amplitude of the $A_g(1)$ mode does not show any pump polarization dependence suggests its equal coupling to both B_{1u} and B_{3u} IR-active modes. In turn, the $A_g(2)$ mode has a stronger coupling to the B_{1u} mode.

In TbFeO₃, the properties of the nonlinear phonon coupling were studied for two crystallographic orientations: *bc* plane (*a*-cut) and *ac* plane (*b*-cut). The comparison of different crystallographic orientations allows for a better understanding of the IR-active phonon excitation and their coupling to Raman-active modes. As expected, the *b*-cut sample of Tb orthoferrite unveiled a similar behavior of the Raman-active phonon modes to those observed for the *b*-cut of ErFeO₃ [see Figs. 3(d) and 3(e)]. Since there is no phase difference in the frequency decomposed data [Fig. 3(e)], both frequencies are related to the symmetric A_g phonon modes. A similar quadratic-linear coupling with equal strength was observed between $A_g(1)$ and B_{1u} (B_{3u}) phonon modes. The $A_g(2)$ mode shows a stronger coupling to the B_{1u} mode as in ErFeO₃. A considerable and unexpected rise in the amplitude of the $A_g(2)$ mode is observed for the pump polarized at $\alpha = 135^\circ$. This behavior cannot be explained by the opposite signs of the coupling constants c_{1R} and c_{2R} related to quadratic-linear coupling terms and remains beyond the simple model based on Eq. (1).

The *a*-cut TbFeO₃, with the *b* and *c* axis lying in the sample plane, enables excitation of the B_{1u} and B_{2u} IR-active modes with a linearly polarized pump pulse. The pump polarization-dependent Fourier spectra in Fig. 3(f) show two phonon modes again. The amplitude and phase of the low-frequency mode (≈ 3.4 THz) are invariant with respect to the pump polarization. Similarly to the *b*-cut samples, the invariance is a signature of the symmetric A_g Raman modes coupled to B_{1u} or B_{2u} mode via the quadratic-linear term. The relatively low amplitude of the $A_g(1)$ mode, as compared to the one observed in the *b*-cut samples, may stem from the different detection conditions. Unlike the *b*-cut samples, which exhibit only a quadratic-linear interaction between the $A_g(2)$ and B_{iu} modes, the simultaneous excitation of B_{1u} and B_{2u} IR-active modes in the *a*-cut TbFeO₃ reveals a trilinear coupling regime of the form $B_{1u}B_{2u}B_{3g}$. It follows from the phase variation of the 4.2 THz Raman phonon as a function of the pump polarization [Fig. 3(g)]. This mode shows a π shift when the pump polarization changes its projection on the *c* axis. Notably, the ≈ 4.2 THz peak on the Fourier spectrum also shows a remarkable increase in amplitude when the pump polarization is parallel to one of the crystallographic axes (*b* or *c*). This behavior indicates that the peak at 4.2 THz corresponds to the two different interactions, trilinear and quadratic linear, and thus two different phonon modes [$B_{3g}(2)$ and $A_g(2)$] for the pump polarized at $\alpha = 45^\circ$ and 0° respectively. Despite the stronger quadratic-linear interactions, which are seen in the spectral density data with the pump polarized along one of the crystallographic directions [Fig. 3(f)], this effect is

TABLE I. Summary of observed Raman phonon modes with a nonlinear coupling mechanism responsible for their excitation.

Phonon mode	Sample			
	ErFeO ₃ (<i>b</i> -cut)	TbFeO ₃ (<i>b</i> -cut)	TbFeO ₃ (<i>a</i> -cut)	TmFeO ₃ (<i>a</i> -cut)
$A_g(1)$ (≈ 3.4 THz)	B_{1u}^2, B_{3u}^2	B_{1u}^2, B_{3u}^2	B_{1u}^2, B_{2u}^2	B_{2u}^2
$A_g(2)$ (≈ 4.2 THz)	B_{1u}^2	B_{1u}^2, B_{3u}^2	B_{1u}^2, B_{2u}^2	B_{1u}^2, B_{2u}^2
$B_{3g}(1)$ (≈ 3.3 THz)				$B_{1u}B_{2u}$
$B_{3g}(2)$ (≈ 4.2 THz)			$B_{1u}B_{2u}$	
$B_{3g}(3)$ (≈ 4.8 THz)				$B_{1u}B_{2u}$

insignificant for the intermediate pump polarization state ($\alpha = 45^\circ$ and 135°) as seen from a complete π shift for the 4.2 THz mode at this polarization [Fig. 3(g)]. Thus, we assume that two orthogonal IR-active modes have opposite signs of the anharmonicity (coupling) coefficients ($c_{1R} = -c_{2R}$). Obviously, the coupling properties between two pump polarization angles $\alpha = 225^\circ$ and 45° are identical.

A comparatively different lattice dynamics was observed in the *a*-cut TmFeO₃ sample. Unlike other orthoferrites studied in this work, the Fourier spectra of the TmFeO₃ sample show an additional phonon mode at ≈ 4.8 THz [Fig. 3(h)]. Besides, the low-frequency mode (≈ 3.2 THz) shows different behavior in TmFeO₃, having a maximum amplitude for the pump polarized at 45° . Based on the phase dependence on the pump polarization observed for this mode in the frequency decomposed data [Fig. 3(i)], we conclude that the low-frequency phonon mode in TmFeO₃ originates from the trilinear coupling mechanism and is identified as an antisymmetric phonon mode [$B_{3g}(1)$]. Despite this, the quadratic-linear coupling between the IR-active (B_{2u}) and Raman-active [$A_g(1)$] modes with a similar to $B_{3g}(1)$ frequency manifests itself, which can be seen on the corresponding Fourier spectra [Fig. 3(h)] when the pump is polarized along the *b* axis ($\alpha = 90^\circ$). Thus, two coupling mechanisms are responsible for the low-frequency dynamics.

The second phonon mode with a characteristic frequency of ≈ 4.2 THz is simply a symmetric $A_g(2)$ mode excited through the quadratic-linear interaction, mainly with the IR excited B_{1u} mode. Indeed, this mode does not show any significant amplitude or phase variation regarding the pump polarization.

The amplitude of the high-frequency mode, located at ≈ 4.8 THz, shows a pump polarization dependence similar to that of the low-frequency mode, with a maximal amplitude of oscillation when the pump is polarized at 45° . At the same time, it shows a decrease in the oscillation amplitude when the pump polarization is aligned with one of the crystallographic axes. Such behavior indicates a minor contribution from quadratic-linear coupling, leaving only a trilinear coupling as the mechanism responsible for the mode

excitation. Thus, the high-frequency mode is an antisymmetric $B_{3g}(2)$ phonon excited through the trilinear coupling with B_{1u} and B_{2u} phonons. Similar to the *a*-cut TbFeO₃, the signals for the pump polarization angles $\alpha = 45^\circ$ and 225° are identical.

The observed phonon modes, their symmetry, and the coupling properties are summarized in Table I for samples with different rare-earth ions and crystallographic orientations. The cross-section cells show whether the given Raman-active mode was observed in the sample and what potential energy term is responsible for the excitation.

IV. CONCLUSION

In this work, we have experimentally investigated the properties of the nonlinear coupling between resonantly excited IR-active and Raman phonon modes in the rare-earth orthoferrites. We have identified their coupling mechanisms and assigned them to a symmetry group. We found that all the highest-frequency IR-active modes $B_{3u}(9)$, $B_{2u}(9)$, and $B_{1u}(7)$ have a strong quadratic-linear coupling with the low-frequency symmetric Raman-active modes $A_g(1)$ and $A_g(2)$. A trilinear coupling was only observed in the *a*-cut samples, implying the vital role of the $B_{2u}(9)$ mode in this coupling regime and revealing selectivity of the trilinear coupling mechanism concerning a particular Fe-O bond stretching involved in the IR-active modes. Our results form a robust basis for future studies of lattice-driven phenomena in the orthoferrites.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [36].

APPENDIX: EXPERIMENTAL SETUP

Schematics of the experimental setup are shown in Fig. 4.

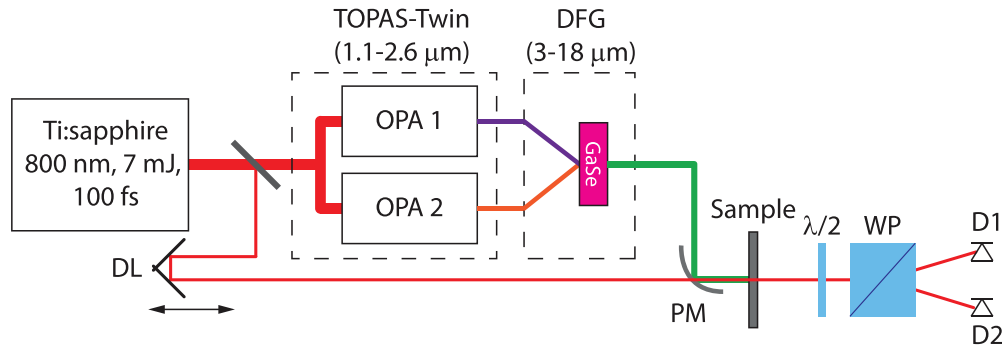


FIG. 4. Schematics of the experimental setup. The output of the Ti:sapphire laser is split into two parts: The majority of energy (90%) is used to generate a MIR pump pulse, and a tiny part of the fundamental laser beam (800 nm) is used as a probe. Outputs of two slightly detuned OPAs were mixed via the nonlinear process of differential frequency generation (DFG) in a GaSe crystal, yielding the MIR pulse, tunable in a 3–18 μm spectral range. Afterwards, the pump was focused on the sample with the parabolic mirror (PM). The probe pulse was guided through the motorized delay line (DL) and also focused on the sample through the parabolic mirror. After transmitting the sample, the transient change in the probe polarization was measured using the polarization bridge, consistent with the half-wave plate ($\lambda/2$), the Wollaston prism (WP), and a pair of photodiodes (D1 and D2).

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