Magnetostuctural coupling in \( R \text{FeO}_3 \) (\( R = \text{Nd}, \text{Tb}, \text{Eu} \) and \( \text{Gd} \))

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We investigate the interplay of magnetization and lattice vibrations in rare-earth orthoferrites \( R \text{FeO}_3 \), with a specific focus on non-symmetry-breaking anomalies. To do so, we study the magnetization, magnon excitations and lattice dynamics as a function of temperature in \( \text{NdFeO}_3 \), \( \text{TbFeO}_3 \), \( \text{EuFeO}_3 \) and \( \text{GdFeO}_3 \). The magnetization shows distinct temperature anomalous behavior for all investigated rare-earth orthoferrites, even in the compounds with no phase transitions occurring at those temperatures. Through spin–phonon coupling, these magnetic changes are mirrored by the \( \text{FeO}_6 \) rotation mode for \( \text{NdFeO}_3 \) and \( \text{TbFeO}_3 \) cases. Our work sheds light into the common magnetostuctural coupling in rare-earth orthoferrites, and the important role of magnetic anisotropy and spin–orbit coupling strength of the \( R–\text{Fe} \) interactions on the spin-reorientation transition at high temperatures.

Rare-earth orthoferrites \( R \text{FeO}_3 \) (\( R = \text{rare-earth trivalent cation} \)), despite being studied for decades\(^1\)\(^–\)\(^4\), attracted recent scientific interest thanks to their intriguing magnetic properties, including spin-reorientation transitions and new-found magnetically induced ferroelectricity\(^5\)\(^–\)\(^12\).

The \( \text{Fe}^{3+} \) spins order at \( T_\text{N} \) between 623 and 740 K, with increasing temperature for increasing rare-earth cation size\(^5\)\(^,12\). The ordering is triggered by the condensation of the magnetic order parameter with symmetry \( m \Gamma_4^* \). This gives rise to an \( A \bar{F} G \bar{z} \)-type ordering of the \( \text{Fe}^{3+} \) spin sublattice (in Bertaut notation)\(^14\) with the magnetic space group \( P\text{n} \text{m} \text{a}' \). The primary magnetic order is of the antiferromagnetic G-type. The canted spin structure leads to a net-magnetization along the \( b \)-axis\(^5\)\(^,14\). The \( R^{3+} \) spin-sublattice orders below 10 K. Like the \( \text{Fe}^{3+} \) spin-sublattice, a G-type order dominates the magnetic structure of the \( R^{3+} \) spin-sublattice. The interaction of both G-type lattices can give rise to improper ferroelectricity, as for instance in \( \text{GdFeO}_3 \) below 3 K\(^9\)\(^,12\)\(^,15\)\(^,16\).

Between \( T_\text{N} \) and the temperature of \( R^{3+} \) spin ordering, the magnetic landscape is dominated by the cross-talk of the ordered iron sublattice and the paramagnetic rare-earth spins. On the one hand, rare-earth ions with a significant magnetocrystalline anisotropy trigger a spin reorientation transition of the magnetic iron sublattice (e.g. \( R = \text{Nd}, \text{Sm}, \text{Er} \) and \( \text{Tb} \))\(^3\). On the other hand, the iron sublattice induces a net magnetization of the rare-earth sublattice. It was suggested that parallel or antiparallel alignment of the \( R^{3+} \) spin sublattice with respect to the \( \text{Fe}^{3+} \) one is steered by the octahedron tilt system, thus linking the crystal structure and magnetism\(^17\).

In this intermediate regime, temperature-dependent magnetic anomalies were reported. For instance, the \( M(T) \) curves of \( \text{GdFeO}_3 \) and \( \text{TbFeO}_3 \) exhibit s-like anomalies at around 210 and 250 K, respectively\(^1\)\(^–\)\(^6\). However, their origins and link to the crystal structure and lattice vibrations remain still unclear.

Our present work is motivated by the need to shed light on these aspects aiming for a deeper understanding of the magnetic behavior in \( R \text{FeO}_3 \). Towards this objective, we scrutinize the magnetization, and Raman-active magnons and phonons across a large temperature range of a series of \( R \text{FeO}_3 \): \( \text{NdFeO}_3 \), \( \text{TbFeO}_3 \), \( \text{EuFeO}_3 \) and \( \text{GdFeO}_3 \). We selected these four compounds for their different rare-earth magnetic properties and interplay between magnetic and lattice degrees of freedom, to allow the access to different magnetic interactions between the \( \text{Fe}^{3+} \) and the \( R^{3+} \) spins. For instance, both \( \text{NdFeO}_3 \) and \( \text{TbFeO}_3 \) exhibit spin-reorientation transitions, yet at different temperatures, and hence a significant magnetocrystalline anisotropy. On the other hand, \( \text{Gd}^{3+} \) ions present no magnetocrystalline anisotropy of spin–orbit origin (i.e. zero orbital moment, with a large spin moment) and \( \text{Eu}^{3+} \) has no magnetic moment. Therefore, this set of compounds is representative for the family of orthoferrites in general. From the comprehensive study of the temperature dependence of the magnetization and...
magnon wavenumbers, different types of magnetic anomalies are ascertained, which are not associated with non-symmetry-breaking. These magnetic changes are mirrored in the FeO₆-rotation and R-oscillation modes, via spin-phonon coupling. Our experimental results show a common magnetostructural effect occurring in these FeO₃, associated with the FeO₆ octahedra rotations, and a cross-talking between Fe³⁺ spins and the R³⁺ spins for the NdFeO₃ and TbFeO₃ cases that exposes the importance of magnetic anisotropy and spin–orbit coupling in triggering the spin-reorientation transition.

Methods
High-quality ceramic pellets of RFeO₃ (R = Nd, Eu, Gd and Tb) were processed through the urea sol–gel combustion method, sintered at 1350 °C for 60 h, quenched to room temperature. X-ray powder diffraction patterns were recorded at ambient conditions using a X’Pert Pro PANalytical diffractometer with a copper anode (1.54184 Å) in Bragg–Brentano geometry and an ultrafast X’Celerator detector with a secondary monochromator, from 10° to 95° in 2θ. Rietveld refinements of the diffraction patterns confirm the correct Prim a space group (see Fig. S1 of Supplemental Material). No secondary phases were detected, except in NdFeO₃ ceramics, which show an amount of 6.8% of Nd₂O₃.

Low-field DC induced specific magnetization measurements were carried out using commercial superconducting quantum interference SQUID magnetometer. The magnetization was measured after zero-field (ZFC) and field cooling (FC) from 5 to 380 K under an applied magnetic field of 40 Oe, with a resolution of 1 × 10⁻⁶ emu.

Raman spectra were recorded using a Jobin–Yvon T64000 spectrometer and a Renishaw inVia Qontor with 514.5 nm and 532 nm linearly polarized excitation lines of Ar⁺ and diode-pumped lasers, respectively. The spectral ranges cover 100 to 800 cm⁻¹ and – 600 to 600 cm⁻¹. Measurements were performed at fixed temperatures from 10 to 875 K using either a closed-cycle helium cryostat or a THMS600 Linkam Stage. The effect of the laser power on the sample was previously studied and it was limited below 5 mW to prevent sample heating. The best fits of a sum of damped oscillators to the measured Raman spectra allow us to determine the wavenumbers of the phonon and magnon modes.

Experimental results and discussion

Magnetic properties and interactions.
In the first step of our study, we investigate the temperature dependence of the magnetization for NdFeO₃ (FC), TbFeO₃, EuFeO₃ and GdFeO₃ (ZFC), as displayed in Fig. 1. The vertical dashed arrows mark the temperatures of anomalies that will be important for the following sections of this work. Remarkably, the magnetization curves have little in common and the magnetization signals are dramatically different for different rare-earths. This motivates the following detailed analysis.

NdFeO₃. The magnetization of NdFeO₃ (Fig. 1a) is temperature independent between 350 and 175 K. With the start of the spin reorientation from AFG, (Pnma) to C2/G,F₆-type order (Pm’n’α) at 170 K, M(T) increases monotonously until a small dent at 110 K marks the end of the spin reorientation regime. Down to 70 K, M(T) further increases. Hereafter, the magnetization decreases due to the gradual antiparallel ordering of the Nd³⁺ spins in the exchange field of the Fe³⁺ spins. At 9 K, the magnetic contributions of the Nd³⁺ and Fe³⁺ spins compensate and the magnetization reverses for lower temperatures. The M(T) profile of the ceramic sample qualitatively agrees with the vector sum of the b-axis and c-axis components of the magnetization for single crystal measurements taken from Ref.7 (see inset of Fig. 1a).

TbFeO₃. In Fig. 1b, M(T) of TbFeO₃ increases with decreasing temperature with changes in slope for several temperature intervals. At 280 K and at 150 K, the slope of M(T) increases slightly (see Fig. S2 of Supplemental Material for a detailed view). These features were reported earlier, however, remain to be understood. Below 20 K, the slope of M(T) becomes steeper with a maximum at 10 K. The sudden increase in slope at 20 K marks the onset of the spin-reorientation transition, where the net magnetic moment of the Fe³⁺ spins rotates from the b- to the c-axis. In addition, the Tb³⁺ spins order in the exchange field of the Fe³⁺ spins below 10 K, reflected by the saturation of M(T) in good agreement with the literature.

EuFeO₃ and GdFeO₃ do not show a spin-reorientation transition. Nevertheless, the M(T) curve of both materials is characterized by anomalies with clear changes in slope. The magnetization of EuFeO₃ increases as the temperature decreases toward its maximum at 30 K, presenting a broad anomaly around 200 K. Also a broad maximum of M(T) around 200 K was reported in the literature for EuFeO₃, with the magnetization decreasing towards 0 K. The temperature dependence of the magnetization of GdFeO₃ is more complex, exhibiting strong variations below 100 K. For T < 36 K, the magnetization increases due to the paramagnetic response of the Gd³⁺ sublattice. Qualitatively, the M(T) curve of GdFeO₃ agrees with the results reported in the literature. The existence of magnetic changes occurring at 260 K is also ascertained by the anomalous temperature dependence of the coercive field at 200 K.

Among the four studied compounds and in the 5 to 350 K range, TbFeO₃ presents the highest maximum magnetization value (around 500 emu/mol), while EuFeO₃ presents the smallest one (around 0.5 emu/mol, 3 orders of magnitude smaller than TbFeO₃). GdFeO₃ and NdFeO₃ are in between, with GdFeO₃ presenting a substantially larger magnetization than EuFeO₃. Therefore, we conclude that the contribution of the Nd³⁺, Gd³⁺, and Tb³⁺ paramagnetic momenta or their interaction with Fe³⁺ add a significant contribution for the overall magnetization. In the case of TbFeO₃ and GdFeO₃, the R³⁺ spins align parallelly to the net magnetization of the Fe³⁺ spins, leading to an increase of the overall magnetization. The Nd³⁺ spins, in turn, align antiparallelly to the Fe³⁺ spins. Hence, the magnetization decreases and even reverses at low temperatures.
Figure 2 summarizes the temperatures where discernable magnetic anomalies are observed for each \( RFeO_3 \). Apart from the spin-reorientations of \( \text{NdFeO}_3 \) and \( \text{TbFeO}_3 \), these anomalies below \( T_N \) do not correspond to any critical phenomena or phase transitions. The observed anomalies in the \( M(T) \) curves, which are between 3 and 4 orders of magnitude larger than the measurement resolution, indicate complex magnetic interactions in the investigated orthoferrites, triggered by the interaction between \( \text{Fe}^{3+} \) and \( R^{3+} \) spins, which we analyze in the following.
In the molecular field approximation, we can express the net magnetization resulting from the interaction of the order Fe$^{3+}$ sublattice and the paramagnetic $R^{3+}$ spins as follows:

$$M(T) = 2\alpha\sigma(T) \left[ 1 + \frac{(d)}{T} \right],$$

(1)

where $\alpha$ is the spin canting angle, $\sigma(T)$ the $Fe^{3+}$ sublattice moment, $(d)$ the mean $R$–$Fe$ interaction parameter and $t = T/T_N$.

$NdFeO_3$ presents two linear regimes above and below the spin reorientation transition. The slope in the 10 to 60 K range is about 59% steeper than above the spin reorientation. We interpret this as a consequence of the emergent magnetic interaction of $Nd^{3+}$ and $Fe^{3+}$ spins below the spin reorientation regime.

$TbFeO_3$ also exhibits two linear regimes in the 20 to 80 K and 250 to 350 K in $F(t)$, respectively, with a slope decrease of about 70% as temperature increases, in agreement with the literature. The deviation below 260 K from the high temperature linear regime can be better observed in the residuals plot obtained from subtraction of the linear fit to the data, shown Fig. S2 of the Supplemental Material.

$EuFeO_3$ exhibits two different linear temperature dependences from 5 to 150 K, and 230 to 350 K, respectively, with only a minor slope change, of the order of 4%. This is in agreement with small variation of magnetization with temperature.

$GdFeO_3$ displays the most complex $F(t)$ behavior, with linear relations from 10 to 35 K, 100 to 150 K and 250 to 300 K and a local maximum at 200 K. Such a behavior suggests that the model does not fully reproduce the magnetic properties of GdFeO$_3$ above 150 K, but this shall not invalidate the calculation of the $(d)$ value at very low temperatures.

The calculated $(d)$ values are presented in Table 1. For the fitting, the linear regime at low temperatures (see Table 1) was used, where the $R$–$Fe$ magnetic interaction is strongest. The $(d)$ values are about one order of magnitude smaller than those reported by Treves, which were calculated from data available only above 100 K.

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![Figure 2](image-url)

**Figure 2.** Magnetic phase sequence for $RFeO_3$ with $R = Nd$, Tb, Eu and Gd. Critical temperatures of the reported phase transitions taken from Refs. 10,15,25. Dashed lines mark relevant anomalies observed in this work on $M(T)$ curves, not associated with phase transitions.

| Compound  | $(d) \times 10^3$ | $\Delta T_{\text{fit}}$ (K) |
|-----------|------------------|----------------------------|
| NdFeO$_3$ | $-10.24 \pm 0.03$ | 11–52                      |
| TbFeO$_3$ | $10.3 \pm 0.1$    | 18–70                      |
| EuFeO$_3$ | $-0.62 \pm 0.05$  | 5–160                      |
| GdFeO$_3$ | $11.3 \pm 0.1$    | 13–34                      |

Table 1. Mean $R$–$Fe$ interaction parameter $(d)$ calculated from the best fit of Eq. (1) to the experimental data shown in Fig. 1a–d, and the temperature interval where the fit is performed.
values. The difference is thus due to the analyzed temperature regime, and we consider that our fittings to the lower temperature range more correctly account the underlying physics.

For NdFeO₃, ⟨d⟩ is negative. This indicates antiferromagnetic interaction between Nd³⁺ and Fe³⁺ spins, in good agreement with the Nd³⁺ spin ordering antiparallel to the Fe³⁺ spins. For GdFeO₃ and TbFeO₃, ⟨d⟩ is positive. This leads to a parallel alignment of Tb³⁺/Gd³⁺ and Fe³⁺ spins and explains the increase in overall magnetization and the absence of a compensation temperature. We note, that these values are in agreement with the theoretical ones for the orientation of the rare-earth sublattice magnetization with respect to the Fe³⁺ spins sublattice. Among the studied compounds, the mean interaction coupling parameter between Eu³⁺ and Fe³⁺ cations has the smallest absolute value. This indicates a comparably small interaction between both ions and can be understood by the small magnetic momentum of the Eu³⁺ cations.

It is worth to stress that, although the values of ⟨d⟩ are similar for both GdFeO₃ and TbFeO₃, the anisotropy of TbFeO₃ is larger, such that TbFeO₃ shows a spin-reorientation transition whereas GdFeO₃ does not. NdFeO₃ and TbFeO₃ show a similar R–Fe interaction parameter ⟨d⟩, yet of different sign. Also, the spin reorientation temperatures differ significantly for both materials. These behaviors underline the complexity of magnetic interactions in rare-earth orthoferrites.

Magnon excitations. We now investigate the magnetic changes through a temperature-dependent analysis of collective spin excitations of the Fe³⁺ spin lattice, so-called magnons. Magnons are known to be an excellent probe of subtle magnetic changes, such as the beforehand reported anomalies in RFeO₃ with R = Y, Sm, Dy, Ho, Er, and Tb.

Figure 3 shows the unpolarized Stokes and anti-Stokes Raman spectra of RFeO₃ (R = Nd, Eu, Gd and Tb), in the −40 to 40 cm⁻¹ spectral range, recorded at 80 and 300 K.

![Representative unpolarized Stokes and anti-Stokes Raman spectra of RFeO₃ (R = Nd, Eu, Gd and Tb), in the −40 to 40 cm⁻¹ spectral range, recorded at 80 and 300 K.](image-url)
available data from the literature between 6 and 300 K for TbFeO₃. We begin by discussing NdFeO₃, shown in Fig. 4a,e, which shows a particularly interesting behavior with several regimes. Between 500 and 240 K, the wavenumber of the magnon M1 increases monotonously with decreasing temperature. From 240 to 100 K, the magnon M1 softens by 1.5 cm⁻¹. In addition, cusp-like anomalies mark the limits of the spin-reorientation temperature range (170–110 K). Below 100 K, the wavenumber of magnon M1 increases upon further cooling. Following the interpretation given for TbFeO₃ and SmFeO₃, this result is associated with the alignment of the Nd³⁺ spins in the exchange field of the Fe³⁺ spin sublattice. Qualitatively, our temperature dependence of M1 wavenumber for NdFeO₃ is in good agreement with the one observed through THz spectroscopy data. Magnon M2 hardens on cooling down to 240 K. At the high temperature limit of the spin-reorientation a cusp-like anomaly occurs and, on further cooling down to 78 K, magnon M2 slightly softens.

The temperature dependence of the M1 and M2 magnons wavenumber of TbFeO₃ here reported (Fig. 4b,f closed symbols) are in good agreement with the already reported data (open symbols), with only the exception of the points between 80 and 100 K, for the case of M1. The wavenumber of both magnons increases monotonously as the temperature decreases. A clear change of slope of the temperature dependence of M1 is observed.

![Figure 4. Temperature dependence of the wavenumber of the magnons M1 (left) and M2 (right) observed in NdFeO₃, TbFeO₃, EuFeO₃, and GdFeO₃. Open symbols for TbFeO₃ were taken from Ref. 27. Vertical dashed lines mark the spin reorientation temperatures following Ref. 13, while dashed arrows mark relevant M(T) anomalies observed in Fig. 1a–d.](image-url)
at around 150 K, in the temperature interval for which the change of slope of the $F(t)$ function is observed (cf. Fig. 1b). The wavenumber of the magnon M2 experiences a sudden increase below 20 K, associated with the spin reorientation transition.

The wavenumber of both magnons of EuFeO$_3$ shown in Fig. 4c–g, increases as temperature decreases and no clear anomalous temperature dependence is found down to 80 K. The temperature dependence of the magnon wavenumbers of GdFeO$_3$ are depicted in Fig. 4d–h. The wavenumber of the magnon M2 increases monotonously as temperature decreases towards 80 K, without any hint of anomalous behavior. However, the wavenumber of M1 increases as temperature decreases from 450 K down to 350 K, then it becomes temperature independent down to 200 K, and on further cooling, the wavenumber of magnon M1 increases linearly down to 100 K.

Among the studied compounds, the magnon wavenumbers of TbFeO$_3$ exhibit the largest temperature variation, reaching more than 6 cm$^{-1}$ for M1, while the smallest variations are found in EuFeO$_3$ and are less than 1 cm$^{-1}$ for M1 and 4 cm$^{-1}$ for the M2 mode, in agreement with their respective largest and smallest magnetization changes (cf. Fig. 1). We can conclude that the anomalies identified in the magnetization curves appear to affect only the M1 mode (seen in TbFeO$_3$ and GdFeO$_3$), while they apparently do not affect the M2 mode, which only presents anomalies at the spin-reorientations (seen in NdFeO$_3$ and TbFeO$_3$). Having in mind the ferromagnetic origin of the M1 magnons, this result points out that the observed magnetic anomalies in TbFeO$_3$ and GdFeO$_3$ might be associated with changes of the ferromagnetic interactions.

Comparing the temperature behavior of the magnons wavenumber in NdFeO$_3$ to other compounds with spin-reorientation, we conclude that M1 exhibits a similar incomplete softening to those reported for ErFeO$_3$, TmFeO$_3$ and SmFeO$_3$, which has been attributed to the coupling between the Fe$^{3+}$ spins and the R$^{3+}$ electronic states$^{30–33}$. In this regard, it seems that M1 has a common temperature dependence for all RFeO$_3$ with spin-reorientation. In contrast, the published results do not exhibit the softening of M2 neither any anomalies seen at the spin-reorientation limits in both magnons wavenumber$^{26,27}$, which deserves further more detailed studies of spin excitations across the spin-reorientations of these compounds.

### Spin–phonon coupling

In the next step, we investigate the response of the phonon spectra as a function of temperature. The optical phonons of the RFeO$_3$ have $A_g$, $B_{1g}$, $B_{2g}$, and $B_{3g}$ symmetries—the mode assignment is available in the literature$^{34}$. Figures 5a–d show unpolarized Raman spectra in the range from 100 to 580 cm$^{-1}$, for NdFeO$_3$, TbFeO$_3$, EuFeO$_3$, and GdFeO$_3$, respectively, measured at fixed temperatures between 10 and 800 K. The room-temperature Raman signature agrees with literature data$^{34}$. With decreasing temperature, the phonon bands sharpen and shift at different rates. As a consequence, some bands become better resolved and visible.

From the study of the temperature evolution of each observed mode, we chose to present and discuss in more detail two modes, which present the most relevant spin–phonon coupling: the [010]$_{pc}$ in-phase FeO$_6$ octahedra rotation mode (Fig. 6a–d), and of the out-of-phase $R$–oscillations modes along the $x$- and $z$-axes (Fig. 7a–d).

As the magnetic super-exchanges in the Fe$^{3+}$ spin sublattice is tightly associated with the Fe–O–Fe bond angle, the FeO$_6$ rotation modes are highly sensitive to magnetic changes of the Fe$^{3+}$ spin sublattice. Moreover, since the $R$–oscillation modes are sensitive to the environment around the R$^{3+}$ cations, we use them as probes of the interaction R–Fe spins interaction. To study the spin–phonon coupling, the phonon wavenumber is compared to the expected anharmonic temperature behavior, obtained from the best fit to the experimental data, above 200 K (for NdFeO$_3$ and GdFeO$_3$) and 300 K (for TbFeO$_3$ and EuFeO$_3$), of the equation$^{35}$

$$\omega(T) = \omega_0 - C \left( 1 + \frac{2}{\epsilon \hbar \omega_0/2k_BT - 1} \right) - D \left( 1 + \frac{3}{\epsilon \hbar \omega_0/3k_BT - 1} + \frac{3}{\epsilon \hbar \omega_0/3k_BT - 1^3} \right),$$

where $\omega_0$, $C$, and $D$ are fitting parameters and $k_B$ is the Boltzmann constant. These fits are given as solid lines in Figs. 6 and 7. It is at first sight surprising that no anomalous temperature dependence is observed at $T_N$ (see Fig. S3 of Supplemental Material), also not found for YFeO$_3$.$^{36}$

In the [010]$_{pc}$ in-phase FeO$_6$ octahedra rotation mode, the spin-reorientation for NdFeO$_3$ reveals itself through anomalies in the temperature dependence of this mode observed in Fig. 6a. Its temperature dependence presents a deviation to higher wavenumbers below 170 K. From 150 to 30 K, the wavenumber linearly increases with decreasing temperature. No anomalous temperature dependence at the low temperature limit of $R$–Fe interactions, which leads to a different spin–phonon interaction. This assumption is actually corroborated by the substantially smaller magnitude of the mean interaction parameter ($\langle d \rangle$) of Eu–Fe sublattices relatively to the remaining compounds, as it can be straight confirmed from Table 1.

We now aim at understanding the cross-talk of the magnetic $R$–Fe interaction with the phonon lattice, as recently observed in SmFeO$_3$.$^{46}$ To do so, we address the out-of-phase $R$–oscillations modes, shown in Fig. 7a–d. In general, three different temperature behaviors of these modes are observed.
Concerning the two Nd-oscillation modes (Fig. 7a), their wavenumbers follow the anharmonic temperature law down to 110 K, below which a small downshift occurs. On further cooling, they both increase linearly, with a maximum downshift of around 0.5 cm⁻¹ at 10 K. Although small, this points out for a coupling between the spin structure and the phonons involving the Nd³⁺ cations.

Figure 7b shows the temperature dependence of the wavenumber of the two Tb-oscillation modes. Below 280 K/150 K, the wavenumber of the Tb(z)/Tb(x) oscillation mode shows a notable upshift/downshift, with a maximum magnitude of 4 cm⁻¹. Each mode starts its deviation at a temperature wherein an anomaly was found in the M(T) curve, evidencing the interaction of the ordered Fe³⁺ spins with the paramagnetic Tb³⁺ spins. Moreover, the different temperature of deviation and direction of the Tb-oscillation modes wavenumber along each crystallographic axis are evidence of a strong magnetic anisotropy which affects the elastic interactions involving the Tb³⁺ cations.

Finally, for EuFeO₃ and GdFeO₃, the wavenumber of both R(z) and R(x)-oscillation modes follow the expected anharmonic temperature dependence in the investigated range, as shown in Fig. 7c,d, respectively. The absence of a coupling between spins and the R-oscillation modes can be understood by the properties of the Eu³⁺ and Gd³⁺ cations. The van Vleck character of Eu⁺⁺ cation leads to a small magnitude of the mean interaction parameter (d) regarding the magnetic Eu⁺⁺–Fe³⁺ interactions, which are therefore small. On other hand, Gd³⁺ does not
exhibit magnetocrystalline anisotropy and, as it has no orbital angular momentum, the spin–orbit interaction is negligibly small. Consequently, a negligible coupling between Gd$^{3+}$ spin orientation changes and cationic oscillations are expected.

To get further information regarding the coupling between phonons and spins, we investigate the quantitative correlation between the measured magnetization and the contribution $\Delta \omega = \omega_{\text{ph}}(T) - \omega_{\text{ph-anhar}}(T)$ to the phonon wavenumber due to changes in the spin structure.

**Figure 6.** Temperature dependence of the [010]$_{pc}$ in-phase octahedra wavenumber for NdFeO$_3$, TbFeO$_3$, EuFeO$_3$ and GdFeO$_3$. The solid curves were determined by the best fits of the anharmonic temperature law above 200 K (for NdFeO$_3$ and GdFeO$_3$) and 300 K (for TbFeO$_3$ and EuFeO$_3$) and its extrapolation down to 0 K$^{35}$. Vertical dashed lines mark the phase transition temperatures following Ref.$^{13}$, while dashed arrows mark relevant M(T) anomalies.
Figure 7. Temperature dependence of the out-of-phase R(x) and R(z)-oscillations wavenumber for NdFeO₃, TbFeO₃, EuFeO₃, and GdFeO₃. The solid curves were determined by the best fits of the anharmonic temperature law above 200 K (for NdFeO₃ and GdFeO₃) and 300 K (for TbFeO₃ and EuFeO₃) and its extrapolation down to 0 K. Vertical dashed lines mark the phase transition temperatures following Ref.13, while dashed arrows mark relevant M(T) anomalies.
The relation between $\Delta \omega$ and the measured magnetization is shown in Fig. 8a–d (see Fig. S4 of Supplemental Material for a wider temperature range). For NdFeO$_3$ (Fig. 8a), two linear regimes are found: one below 165 K encompassing the spin reorientation process, and another below 70 K, during the Nd$^{3+}$ spins ordering process. Apparently, the different slopes of the linear relations result from the different mechanisms involved in each process.

For TbFeO$_3$, a unique linear dependence is observed, from 313 to 25 K. Below 25 K no linearity is observed, which could be associated with precursor effects of the spin-reorientation taking place at 20 K. In EuFeO$_3$ and GdFeO$_3$ (Fig. 8c,d), the unique linear dependence found below 250 K shows that these wavenumbers deviations origin from the magnetic changes, seen here via the spin–phonon coupling. In GdFeO$_3$, this linearity is lost below 100 K, where strong non-monotonous variations of the M(T) curve are observed. This quantitative analysis allows...
us to state that the found magnetostructural effect results from a linear spin–phonon coupling that mediates the [010]pc in-phase octahedra rotational phonon and the magnetic structure.

To further evidence that the Nd(z)- and Tb(z)-oscillation modes are sensing the same phenomena of the [010]pc in-phase octahedra rotation mode, we have studied the correlation between their wavenumbers, shown in Fig. 9. We chose the R(z) instead of the R(x), because for the case of TbFeO₃ only the former shows a deviation similar to the FeO₆ rotation mode. The linear correlations between their wavenumbers found in the analyzed temperature ranges evidence for a coupling between them, with an unknown phenomenologically proportionality constant. For TbFeO₃, around 133 K, within the temperature interval where the slope of the linear temperature dependencies of both the \( F(t) \) and M₁ wavenumber curves changes the most, there is also a change of the found phenomenologically proportionality constant between these modes. This could not be observed in GdFeO₃ due to the absence of coupling between the Gd³⁺ motions and spins.

Conclusions
We have reported an experimental study of the magnetization, Raman-active spin excitations and lattice dynamics in RFeO₃ (\( R = \text{Nd, Eu, Gd, and Tb} \)) in the 10 to 850 K range. The main outcomes are summarized in the following.

Besides the known spin-reorientation of NdFeO₃, anomalies in the temperature dependence of magnetization and wavenumber of both the magnons and the FeO₆ rotation modes evidence for magnetic changes in TbFeO₃, EuFeO₃, and GdFeO₃, between 25 and 350 K, which are not associated with symmetry breaking nor magnetic phase transitions. The reinforcement of the ferromagnetic response of TbFeO₃ and GdFeO₃ is evidenced by both the increasing of magnetization as temperature decreases, and the anomalous temperature behavior of the ferromagnetic mode (magnon M₁) at specific temperatures.

The sensitivity of the optical phonons to the Fe–Fe and \( R – \text{Fe} \) magnetic interactions was evidenced. The linear dependence on the magnetization of the anomalous contribution to the phonon wavenumber, just below the temperature where anomalies in M(T) are observed, distinctly bears the coupling between the [010]pc in-phase octahedra rotation mode and the spin structure, through a linear spin–phonon coupling. Thus, the second main outcome concerns the common magnetostructural coupling, evidenced by FeO₆ octahedra rotations. Like the FeO₆ rotational modes, the Raman-active R-oscillation modes are sensitive to the R–Fe magnetic interactions, provided a strong spin–phonon coupling mediated by spin–orbit coupling. In NdFeO₃ and TbFeO₃, wherein spin–orbit coupling of the R-cations exists, R-oscillations are coupled to the [010]pc in-phase octahedra rotational modes. The experimental results give strong evidence for the cross-talk between Fe³⁺ and Nd³⁺/Tb³⁺ spin sublattice, denoting the third main outcome of this work. The largest variations of the magnon M₁ and both studied Raman modes are the largest for TbFeO₃. Moreover, the smaller spin–phonon coupling strength found for the Nd-oscillations in NdFeO₃ suggests that the anisotropy of the Nd–Fe interaction plays a more important role on triggering the spin-reorientation at higher temperatures rather than its strength. Contrarily though, no deviation
of these two modes could be observed for GdFeO₃, demonstrating the key role played by the spin–orbit coupling to underlie the interplay between spins and the Gd-oscillation phonon.

Data availability
The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.

Received: 22 March 2022; Accepted: 20 May 2022
Published online: 11 June 2022

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Acknowledgements
We are deeply acknowledged to J. L. Ribeiro for the fruitful discussion regarding the interpretation of the magnetic data, and P. Bouvier suggestions on the analysis of some specific phonons. We acknowledge funding from NORTE-01-0145-FEDER-022096, UID/NAN/50024/2019 and PTDC/NAN-MAT/28538/2017 projects and R.V. to the grant from PTDC/NAN-MAT/0098/2020.

Author contributions
P.T. produced the samples. R.V. performed magnetization measurements. R.V., M.W. and A.M. performed Raman spectroscopy measurements. C.D. wrote an algorithm for Raman spectra analysis. R.V., M.W., M.G., J.K., A.A. and J.M. wrote the main manuscript text and R.V. prepared figures. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-022-13097-1.

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