Role of rare-earth ionic radii on the spin-phonon coupling in multiferroic ordered double perovskites

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Abstract
In this paper, we investigated the influence of rare-earth ionic radii on spin–phonon coupling in RE₂NiMnO₆ double perovskites by Raman spectroscopy. Spin–phonons in dense Nd₂NiMnO₆ and Gd₂NiMnO₆ ceramics were investigated by Raman spectroscopy at low temperatures. The magnitude of the observed coupling in comparison with other isostructural compounds shows that coupling is not influenced by the rare-earth ionic radius, as well as the deviation in position of the stretching phonon in the ferromagnetic phase in relation to the anharmonic contributions follows a power law.

1. Introduction

Rare-earth based manganites with double perovskite structure have been intensively investigated in the last decade since the discovery of magnetocapacitance in La₂NiMnO₆ (LNMO) by Rogado et al [1]. This compound is a multiferroic with a Curie temperature near room temperature ($T_C \sim 280$ K), which permits its application in devices whose magnetic properties can be controlled by an electric field.

Since then, intense attention has been given to electric and magnetic properties of LNMO in several kinds of samples, such as ceramics, single crystals, nano-powder, and thin films [2–8]. In addition, a large spin–phonon coupling in thin films of LNMO was observed [9, 10], which it is an important feature for magnetoelastic applications. However, investigations about spin–phonon coupling were mostly focused in LNMO; while, important questions remain open for other compounds of the family, as if the magnitude of spin–phonon coupling depends on rare-earth ionic radii.

In addition to La₂NiMnO₆, spin–phonon coupling has already been observed in Pr₂NiMnO₆ (PNMO) [11], Tb₂NiMnO₆ (TNMO) [12], and Y₂NiMnO₆ (YNMO) [13], all in ceramic samples. In the TNMO case, the authors observed a weak spin–phonon coupling, which could not be observed in the stretching phonon position, as usually observed in double perovskite, but just in its linewidth [12]. They attributed the weak effect to the increase of rare-earth ionic radii. However, the effect was stronger in YNMO [13], similar to that observed in PNO. That result suggested the ionic radii did not strongly influence the spin–phonon coupling magnitude. Recently, spin–phonon coupling observations in Gd(Co,Mn)O₃ suggested that the B-site order in a double perovskite is the main parameter influencing spin–phonon coupling [14], as expected once the occupational disorder in this site increases the antiferromagnetic interactions through a superexchange mechanism. In this paper, we investigated the ceramics Nd₂NiMnO₆ (NNMO) and Gd₂NiMnO₆ (GNMO), synthesized at similar conditions of YNMO [13], in order to determine the ionic radii influence on spin–phonon coupling magnitude in rare-earth–based manganites with double perovskite structure.
2. Experimental methods

Polycrystalline samples of NNMO and GNMO were synthesized by a solid-state route according to a stoichiometric mixture of RE₂O₃, NiO, and MnO oxides. The samples were calcined 10 times at 1000 °C for 12 h. The samples were grounded in an agatha mortar and sieved to obtain a homogeneous powder between each calcination. Finally, the samples were sintered at 1400 °C for 48 h. The crystalline structures were probed by x-ray powder diffraction using a Bruker diffractometer model D8 Advance, in a continuous scanning mode using Cu-Kα radiation (40 kV, 40 mA, 0.02 °s⁻¹). The phases were refined using the Fullprof suite [15]. The refined x-ray powder diffraction patterns obtained for NNMO and GNMO showed that both compounds exhibit an ordered monoclinic-distorted double perovskite lattice, which belongs to the P2₁/n space group, as shown in figure S1 of the supplementary material. The refined structure parameters are in excellent agreement with those obtained previously by Yang et al [16], as well as with those predicted by SPuDs code [17]. The refinement and structural parameters are summarized in table S1 (see supplementary material). Virtually unavoidable traces of starter oxides were detected as secondary phase, which are routinely observed in the synthesis of rare-earth mixed perovskites [12, 13], and are indicated as * in figure S1. It is important to point out that the Ni-O-Mn angle in both compounds favors the superexchange interaction.

Magnetic measurements were carried out in a quantum design (QD) superconducting quantum interference device (SQUID). Temperature sweeps were collected with 4 cm long reciprocating sample option scans. The temperature-dependent magnetization and susceptibility reciprocal of NNMO and GNMO (see figure S1 of the supplementary material) clearly show that both samples exhibit ferromagnetism around T_C = 150 K and 210 K, respectively, which agree with the result obtained by Booth et al [18], and a low coercive field. Low coercive fields usually imply double perovskites with high B-site ordering. Also, the absence of a second magnetic transition below the observed T_C indicates the order is NNMO and GNMO is high, as obtained for YNMO prepared under the same conditions [13].

Raman spectroscopy measurements were performed using a Jobin-Yvon T64000 triple spectrometer configured in a backscattering geometry coupled to an Olympus Microscope model BX41 with a 20x achromatic lens. An Innova coherent laser operating at 100 mW emitting in a 514.5 nm line was used to excite the Raman scattered signal, which was collected in a N₂-cooled CCD detector. All slits were set up to achieve a resolution lower than 1 cm⁻¹. Low-temperature measurements were performed by using a closed-cycle He cryostat where the temperature was controlled to within 0.1 K.

3. Results and discussion

Figures 1(a) and (b) show the low-temperature Raman spectrum of NNMO and GNMO at 40 K. We observed eight and four modes for NNMO and GNMO, respectively. For this monoclinic structure, there are 24 Raman-active modes, which can be described based on the oxygen octahedra internal modes as [19]:

\[ 6T (3A_g \oplus 3B_g) + 6L (3A_g \oplus 3B_g) + 2\nu_1 (A_g \oplus B_g) + 4\nu_2 (2A_g \oplus 2B_g) + 6\nu_3 (3A_g \oplus 3B_g), \]

where L (librational) and T (translational) are lattice modes, while \( \nu_1, \nu_2, \) and \( \nu_3 \) are oxygen octahedra internal modes, which are expected to be observed for wavenumbers higher than 380 cm⁻¹. The observed modes can be assigned based on normal mode calculations for La₂CoMnO₆ [20] and Gd(Co,Mn)O₃ [14], as well as in other double perovskite manganites previously measured [13]. Thus, for NNMO, the symmetric (\( \nu_1 \)) and antisymmetric (\( \nu_2 \)) were observed at 658 and 449 cm⁻¹ respectively, while the bending was observed at 521 cm⁻¹. In the GNMO case, the symmetric (\( \nu_1 \)) and antisymmetric (\( \nu_2 \)) were observed at 650 and 465 cm⁻¹ respectively, while the bending was observed at 518 cm⁻¹. However, it is important point out the significant difference between the number of modes observed for NNMO and GNMO. As reported in the YNMO case, GNMO (eight modes observed) shows a higher number of modes compared to NNMO (just four modes observed). This result confirms the higher lattice monoclinic distortion for compounds with rare earths with low ionic radii. GNMO and YNMO (observed 13 Raman-active modes) [13] show a clear splitting of the modes that originated from cubic aristotopic symmetry. A summary of the observed Raman-active phonons is given in table SII of the supplementary material.

The temperature-dependent Raman spectra of NNMO and GNMO are depicted in figures 1(c) and (d). As usual in double perovskite manganites that do not undergo structural phase transitions, no anomalies were observed in the investigated temperature range [12–14, 21, 22]. The temperature dependence of the stretching phonon positions is shown in figure 2 for NNMO and GNMO. Usually, under temperature changes, the position of the phonon follows Balkanski’s model, which considers the anharmonicity contributions according to the expression
\[
(T) = \omega_o - C \left[ 1 + \frac{2}{\left( e^{\omega_b / k_B T} - 1 \right)} \right] 
\]  

(1)

with \( C \) and \( \omega_o \) being fitting parameters. When considering \( \nu_1 \) stretching mode, the behavior deviates considerably from Balkanski’s model below the Curie temperature of the samples, as shown in figure 2.

This effect is similar to that observed in other ferromagnetic manganites, and it is associated with phonon renormalization induced by magnetic ordering \([9, 11–14, 22]\) due to coupling between magnetic ordering and lattice. According to Granado \textit{et al} \([23]\), in absence of magnetostriction effects and electronic states renormalization, the contribution of spin–phonon coupling \((\Delta \omega_{\text{ph}}) \) to position change of the \( k \)th phonon is approximately given by

\[
\left( \Delta \omega_{\text{ph}} \right)_k \approx - \sum_{i,j>i} I_{ij} \langle S_i \cdot S_j \rangle 
\]  

(2)

where \( I_{ij} \) is the superexchange integral and \( \langle S_i \cdot S_j \rangle \) is the spin correlation function. This contribution, considering only first-neighbor interactions and a molecular field approximation, can be considered in the case of the stretching phonon, as

\[
\left( \Delta \omega_{\text{ph}} \right)_{\text{stret}} \propto \left( \frac{M(T)}{M_s} \right)^2 
\]  

(3)

where \( M(T) \) is the magnetization at the temperature \( T \), and \( M_s \) is the maximum magnetization. The insets in figure 2 show the temperature dependence of the deviation from the anharmonic behavior of the stretching bands for NNMO and GNMO compared with \( \left( \frac{M(T)}{M_s} \right)^2 \) obtained from figure S2. We can see, at temperatures near the magnetic transitions, the model agree very well with experimental data.
Comparing the spin–phonon coupling magnitude in RE$_2$NiMnO$_6$ ceramics for RE = Nd and Gd (this work) with that for RE = Pr [11], Y [13], and Tb [12], the results suggest that the ionic radii do not influence significantly the spin–phonon coupling, with its magnitude being mainly controlled by the B-site ordering, as suggested by Filho et al [13]. Figure 3 shows a comparison considering temperature and wavenumber normalized for RE = Nd, Gd, and Y [13]. Also, we showed the behavior for RE = La [10] and Pr [11] for the sake of comparison. In this plot, the scales were renormalized following the changes $T \rightarrow T/T_C$ and $\omega \rightarrow \omega/\omega (T = 0)$. As we can see, for these all compounds, the spin–phonon magnitude, here measured as $\Delta \omega_{\text{max}}$ in the normalized plot, is around 0.5% of $\omega_p$ for all compounds, being the differences within the resolution limit.

It is important to point out that in the ferromagnetic phase the deviation from the anharmonic behavior follow a power law with the form

$$\Delta \omega \propto \left(1 - \frac{T}{T_C}\right)^\gamma$$

as evidenced by dashed lines in figure 3 ($T < T_C$). For all fitted compounds $1.3 < \gamma < 1.8$, suggesting a universal behavior independent of the rare-earth ion or, in other words, independent of the unit cell size. The parameter $\gamma$ is a normalized order considering that the spin–spin correlation function $\langle S_i \cdot S_j \rangle$ can be described by mean field theory. This power law behavior is similar to that observed for SmCrO$_3$ orthocromite, as shown by Amrani et al [24] for transverse optical phonons.
4. Conclusions

In this paper, we showed that rare-earth manganites RE$_2$NiMnO$_6$ with double perovskite structure present a spin–phonon coupling whose magnitude is independent of the rare-earth ionic radius. In addition, the deviation of stretching phonon position in the ferromagnetic phase with relation to anharmonic contributions follows a power law, whose order parameter is also independent of the rare-earth ionic radius.

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