Short-range antiferromagnetic interaction and spin-phonon coupling in La$_2$CoMnO$_6$ double perovskite

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Abstract

Weak antiferromagnetic (AF) interaction in the ferromagnetic (FM) partially ordered La$_2$CoMnO$_6$ (LCMO) was detected by Raman spectroscopy by monitoring spin-phonon coupling. Because of the sensibility to probe short-range disorder and lattice modifications, the Raman spectroscopy showed to be an useful tool to indicate less remarkable magnetic transitions in LCMO compound. Apart from the expected spin-phonon coupling due to the long-range FM superexchange (T$_c$ ~230 K), phonons parameters pointed out an additional spin-phonon coupling related to the short-range AF interaction at T$_c$ ~135 K, which was not detected from the magnetic bulk response. These results reinforce the Raman spectroscopy as a powerful technique to detect antisite disorder into A$_2$B'B''O$_6$ magnetic double perovskites, whose magnetic properties are driven by superexchange interactions.

Keywords: Raman spectroscopy; spin-phonon coupling; double perovskites; antisite disorder
1. Introduction

Multiferroics with a crystalline structure derived from the $\text{RE}_2\text{Me}^{2+}\text{MnO}_6$ family of double perovskites, where RE and $\text{Me}^{2+}$ are rare earth and transition metal ions, respectively, have attracted much attention due to their peculiar electric and magnetic properties, which involve giant dielectric constant ($>10^3$) [1,2], magnetoresistance [3], magnetocaloric and magnetodielectric effect [3–5], relaxor behavior [6,7], among others. $\text{La}_2\text{CoMnO}_6$ (LCMO) and $\text{La}_2\text{NiMnO}_6$ (LNMO) are good examples of these materials, which, in addition to presenting the above characteristics, have a Curie point near room temperature, around 230K and 280K, respectively, so they are suggested for applications in electrically readable magnetic data storage, spintronic devices and, more recently, for high-performance supercapacitors [3,8–10].

Structural disorder in complex perovskites plays an essential role because it strongly affects their physical and chemical properties. For example, phonons and, consequently, the dielectric response (in the microwave electromagnetic range) are strongly influenced by the antisite disorder in perovskites with 1:2 cation order ($\text{A}_3\text{BB}'_2\text{X}_9$) [11–14]. Also, in $\text{Ba}_3\text{CaNb}_2\text{O}_9$, the high antisite disorder favors the conductivity, enabling its application as protonic conductors [15]. Particularly in $\text{RE}_2\text{Me}^{2+}\text{MnO}_6$ perovskites, the order is critical because, in such materials, the ferromagnetic behavior is driven by the superexchange interaction between $\text{Me}^{2+}$ (partially filled e$_g$ orbital) and $\text{Mn}^{4+}$ (filled t$_{2g}$ orbital) mediated by the oxygen. Thus, disorder generates antisite defects of the type $\text{Me}^{2+} – \text{O} – \text{Me}^{2+}$ and $\text{Mn}^{4+} – \text{O} – \text{Mn}^{4+}$, which induce short-range antiferromagnetic interactions, decreasing the overall ferromagnetic state. High ordered $\text{RE}_2\text{Me}^{2+}\text{MnO}_6$
single crystals exhibit narrow hysteresis (or low coercive field) and only one ferromagnetic (FM) transition, showing only a smooth magnetization at low temperatures.

Commonly, the coexistence of two phases, oxygen vacancies, mixed-valence and antisite defects promotes multiple magnetic interactions at low temperatures, as well as a low saturation magnetization and high coercive field. In the case of LCMO, one of the most ordered polycrystalline sample reported had a magnetization of 5.89 μB/f.u. (formula unit), really close to the theoretical saturation magnetization of 6.0 μB/f.u for a fully ordered sample, a relatively weak coercive field of 2.9 kOe, and only one magnetic transition at \( T_c = 235 \text{ K} \) [16]. On the other hand, LCMO samples processed at very high temperatures (\( T > 1200 ^\circ\text{C} \)) tend to be oxygen-deficient [17–22]. The presence of oxygen vacancies introduces Mn\(^{3+}\) and Co\(^{3+}\) ions which interact ferromagnetically through a vibronic e\(^1\)-O-e\(^1\) superexchange interaction with small stabilization and lower Curie temperature \( (T_{c2}) \) and high coercitivity (~10 kOe) [16,18,23–25]. Moreover, structural ordering influences dielectric [26,27], vibrational [16,19] and electronic properties [21]. Wherein, oxygen content, charges, and antisite defects can be tuned by the synthesis conditions [16–19,26,27].

Raman scattering is a powerful probe to detect the disorder in 1:2 complex perovskites because the two-phonon mode behavior is usually observed, which is induced by the disorder and characterizes the presence of the antisite defects. However, the observation of antisite occupation in 1:1 ordered samples, mainly in RE\(_2\)Me\(^{2+}\)MnO\(_6\) perovskites, is difficult because of the absence of the two-phonon mode behavior. In fact, due to the charge difference between Me\(^{2+}\) and Mn\(^{4+}\) ions, the octahedral modes are related mainly to the Mn\(^{4+}\) ions, as reported by Silva et al. [28]. The two-mode behavior
is only observed when there is a high difference in mass of the metallic ions [29], which is not the case for RE₂Me²⁺MnO₆ perovskites. For LCMO, for example, the spectra of the ordered and disordered samples are very similar, as can be verified in Ref. [16]. However, these compounds usually present strong coupling between magnetic order and phonons, which is easily probed by the Raman spectroscopy through both the position and linewidth of the phonon associated with the MnO₆ stretching [30–36].

In this paper, we exploit the coupling between phonons and magnetic ordering to detect low concentration of antisite defects in magnetic double perovskites using Raman spectroscopy. Thus, this analysis proved to be efficient in detecting the competition between the main FM ordering and short-range antiferromagnetic interactions. For this purpose, we used a partially disordered LCMO ceramic obtained by the polymeric precursor method as a prototype sample. To support our proposal, magnetic, X-ray Photoelectron Spectroscopy (XPS) and X-ray diffraction techniques were also employed.

2. Experimental

Polycrystalline samples of LCMO were produced through the polymeric precursor method [16,37][37]. Wherein cobalt acetate tetrahydrate (C₄H₆CoO₄·4H₂O, Sigma Aldrich), manganese nitrate hydrate (MnN₂O₆·xH₂O, Sigma Aldrich) and lanthanum oxide (La₂O₃, Sigma, Aldrich) were added to an aqueous solution in stoichiometric amounts. The mixture was kept under stirring for about 2 h to obtain a resin, followed by heating treatment at 400 °C to remove the solvent and the organic matter. The starting powder was ground in an agate mortar and heated at 1100 °C for 16 h. Then, the obtained powder
was reground and annealed for 16 h at 1100 °C to obtain the LCMO sample. The crystalline structure of the sample was analyzed by applying the X-ray powder diffraction technique using a Bruker D8 Advance with Cu-Kα radiation (40 kV, 40 mA) over the range from 20° to 100° (0.02 °/step with 0.3 s/step). The structure was refined using the GSAS code [38–40][39,40]. X-ray Photoelectron Spectroscopy (XPS) measurements were performed in a VG ESCALAB 220i-XL system, using Al-Ka radiation and under the pressure of 2×10⁻¹⁰ mbar. Survey XPS spectra were collected with a pass energy of 50 eV, and detailed spectra around the Co 2p and Mn 2p regions were taken with 20 eV pass energy. Magnetic measurements were carried out using a Superconducting Quantum Interference Device (SQUID - Quantum Design), and the temperature sweeps were collected with 4 cm long Reciprocating Sample Option scans. Raman spectroscopy measurements were performed using a Jobin-Yvon T64000 Triple Spectrometer coupled to an Olympus Microscope (model BX-41) equipped with a 20x (long work distance) achromatic lens, which was configured in backscattering geometry. The 514.5 nm line of an Innova Coherent laser operating at 18 mW was used to excite the Raman signal, which was collected in a N₂-cooled CCD detector. All slits were set up to attain a resolution lower than 1 cm⁻¹. Low-temperature measurements were performed by using a closed-cycle He cryostat with a temperature control accuracy of 0.1 K.

3. Results and Discussion

The X-ray powder diffraction pattern obtained from LCMO sample at room temperature is shown in Fig. 1 (a). It was indexed based on a monoclinic unit cell with symmetry belonging to the space group P2₁/n, coherent with a quite ordered sample
[16,18]. The refined structure parameters are in excellent agreement with both previous studies in isostructural compounds obtained by solid-state reaction [41] and theoretical results calculated by the SPuDS program [42].

![Image of X-ray powder diffraction pattern of LCMO ceramic.](image)

**Fig. 1** – (a) X-ray powder diffraction pattern of LCMO ceramic. The solid red line is the fit using the Rietveld method, and the solid green line is the residual between the experimental and calculated patterns. (b) FC and ZFC magnetization with a field of 100 Oe. The inset shows the hysteresis curve at 10 K. (c) XPS spectra of the partially disordered LCMO (black filled squares) for the (c) Co 2p and (d) Mn 2p energy regions.

**Fig. 1** (b) shows the temperature-dependent magnetization of LCMO. The Field-cooled (FC) and the Zero-field-cooled (ZFC) magnetization data were acquired under a
field of 100 Oe (10 mT). These magnetization curves are irreversible below $T < 226$ K, and the apparent divergence between FC and ZFC curves is an indication of the magnetic frustration due to competition between the ferromagnetic and antiferromagnetic interactions, implying a spin-glass behavior [43]. The magnetization curve reveals the onset of the net magnetic moment near 226 K, i.e., the Curie temperature, consistent with previous magnetic measurements in LCMO [16,44,45], and any second FM transition was observed [46,47]. The inset of Fig. 1(b) shows the hysteresis loop at 10 K, and magnetization value tends towards the saturation magnetization value of $\sim 3.49 \mu_B$/f.u. An abrupt change in $H_C$ (coercive field) is observed. Similar effects have been observed in isostructural and related perovskites, where the inhomogeneous concentration of defects and antiphase boundaries (APB) domain borders lead to the strongly pinned magnetic domain walls [48–50].

Magnetic measurements have been used to estimate the B-site structural order in LCMO. Previous works have shown that the structural order level of B-site depends sensitively on their synthesis conditions and can be adjusted as a function of the calcination temperature in air atmosphere [16,21], wherein the sample obtained at 1000 °C had the best order level, with $T_c \sim 235$K and saturation magnetization of $5.89 \mu_B$/f.u. (matching to a nearly stoichiometric ordered sample that contains $\text{Co}^{2+}$ and $\text{Mn}^{4+}$ cations) [16,21]. According to Blasse’s model [51], which purposes to estimate the structural B site ordering using the experimental and theoretical saturation magnetic moments ratio (called $\delta$), this magnetization would correspond to $\delta =0.98$, or about 1% of antisite defects. Thus, for observed saturation magnetization of $3.49 \mu_B$/f.u. (see inset of Fig. 1(b)), we have a $\delta=0.58$, corresponding to 21% of antisite defects. Despite the high number of
antisite defects, the obtained magnetization curve shows only a prominent ferromagnetic transition at 226 K. This transition is usually attributed to long-range ferromagnetic (FM) interaction due to the superexchange interaction between Mn$^{4+}$-O-Co$^{2+}$, stabilized by a stoichiometric oxygen concentration. Dass et al.[18] showed that the stoichiometric compound has a single evident magnetic phase with $T_c = 226$ K (high $T_c$) and $M_s = 5.78(2)$ $\mu_B$/f.u. Oxygen deficiencies stimulate the appearance of Co$^{3+}$ ($t^5e^1$) and Jahn-Teller Mn$^{3+}$ ($t^3e^1$) ions, which generate a vibrionic superexchange FM interaction, but with a lower exchange stabilization and a lower critical temperature (low $T_c$). Multiple magnetic transitions are common in compounds heated above 1200°C in air [17–22].

XPS measurements were carried out to evaluate the oxidation states of Co and Mn ions in partially ordered LCMO as observed in Fig. 1 (c) and (d). Fig. 1(c) shows the Co 2p spectrum with the prominent peaks located at 780.2 eV, for Co 2p$_{3/2}$, and 796.3 eV, for Co 2p$_{1/2}$, whereas the Co 2p$_{3/2}$ peak is observed at 780.5 eV for CoO [52] and the weaker satellite peak observed at 787.1 eV are also features of CoO [53]. Thus, this analysis indicates the dominance of Co$^{2+}$ species [54,55]. Fig. 1(d) shows the Mn 2p spectrum. Considering that the main XPS peak of MnO$_2$, Mn 2p$_{3/2}$ peak, is observed at 642.2 eV [52,55,56], the peaks observed at about 642.4 eV and 654.0 eV can be associated with Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively. Also, these result it is very similar that reported for a very high ordered polycrystalline LCMO sample [16], and together with the magnetic measurement analysis, ruled out the possibility of a significant amount of Co$^{3+}$ and Mn$^{3+}$. Moreover, they confirm that the low saturation magnetization is due to the antiferromagnetic interactions (AFM) promoted by defects of antisite Mn$^{4+}$–O–Mn$^{4+}$ or Co$^{2+}$–O–Co$^{2+}$, and the interaction between APB that occur between regions with AFM
interactions, $\text{Mn}^{4+} - \text{O} - \text{Mn}^{4+}$ or $\text{Co}^{2+} - \text{O} - \text{Co}^{2+}$, or between FM regions promoting AFM interactions in the contours.

The room-temperature Raman spectrum of the LCMO is shown in Fig. 2(a). The spectrum is typical of a manganite with a double perovskite structure and is in excellent agreement with previous works [19,57]. According to Ref. [57], the more intense phonon band, at 646 cm$^{-1}$, corresponds to the (BO$_6$) octahedral symmetric stretching (SS) mode, whereas the mode at 499 cm$^{-1}$ is assigned as a combination of both asymmetric stretching (AS) and bending modes. The low-intensity vibrational modes, observed at 426 and 254 cm$^{-1}$, are associated with the octahedral bending mode, with La moving in the xz plane, and the octahedra out-of-phase tilting vibration along the x-axis, with La and apical O moving in the xz plane, respectively. Furthermore, the two modes at high wavenumbers, i.e., at 1160 and 1283 cm$^{-1}$, are related to the combination of the symmetrical stretching and bending modes and the symmetrical stretching vibration overtone, respectively. The low-intensity modes are shown in the inset of Fig. 2(a).
**Fig. 2** – Raman spectrum of LCMO at room temperature. The inset shows the low wavenumber region of the spectrum. Temperature-dependent Raman-active phonon spectra of LCMO in the wavenumber range of (b) (Co/Mn)O$_6$ symmetric stretching (SS) region and (c) (Co/Mn)O$_6$ asymmetric stretching (AS) and bending mode.

The temperature-dependent Raman spectra of LCMO between room temperature and 40 K are shown in Figs. 2 (b-c). Usually, a spin-phonon coupling in similar double perovskites is observed in octahedral stretching vibrational modes [30,32–34]. The temperature dependence of these modes is shown in Fig. 3 (a-b). The expected anharmonic contribution to the temperature dependence of a phonon position modeled by Balkanski [58] is given by

$$\omega(T) = \omega_0 - C \left[ 1 + \frac{2}{e^{\hbar \omega_0 / k_B T} - 1} \right]$$

with $C$ and $\omega_0$ being the fitting parameters. In the absence of structural phase transitions, as it happens in LCMO, the temperature dependence of the phonons must follow this behavior. However, it is clear that the stretching phonon exhibits a marked deviation from the anharmonic model, which is similar to that recently observed in LCMO [59], as well as for other double perovskites with magnetic transitions, and it is associated with the renormalization of the phonons induced by the magnetic ordering [30,32–35,57,60,61]. The coupling temperature coincides with the start of the magnetic ordering, as shown by the spontaneous magnetization of LCMO (see Fig. 1 (b)).
Fig. 3 – (a-b) Temperature dependence of the symmetric (a) and antisymmetric stretching (b) wavenumbers observed for LCMO (blue spheres). The red lines show the usual behavior of the anharmonic effect contribution to the temperature dependence according to Balkanski’s model. This line is not a fit in the temperature range in which the sample is ferromagnetic (in this region, it is an extrapolation following Balkanski’s model). (c) Difference between AS and SS modes wavenumbers. Temperature dependence of full width at half maximum (FWHM) of the (d) SS (e) AS modes. (f) Temperature dependence of the departure from the anharmonic behavior of the mode that exhibits the spin-phonon coupling compared with $(M(T)/M_0)^2$.

The AS mode also exhibited an anomalous softening near the main magnetic transition (high-Tc), consistent with the reported spin-phonon coupling. However, we can also notice a small second discontinuity at about 135 K (see Fig. 3 (b)). In addition, the frequency difference between the SS and AS modes $\omega_{SS} - \omega_{AS}$ showed three distinct
regions, with changes at about 226 and 135 K (see Fig. 3 (c)). As reported previously, this frequency difference is usually used as a comparative parameter of ordering [16].

The previous characterization already clarified that the LCMO sample is partially disordered with Co$^{2+}$ and Mn$^{4+}$ cations. However, it is well known that, depending on structural order or oxygen content, LCMO can show two or more remarkable magnetic transitions due to: (I) a long-range FM superexchange Mn$^{4+}$-O-Co$^{2+}$, with high $T_c \approx 230$K; (II) a second FM interaction between the intermediate-spin Co$^{3+}(t^5e^1)$ and the Jahn-Teller Mn$^{3+}$ cations, created by the introduction of oxygen vacancies, with secondary low $T_c$ [18,23,62]; (III) AFM interactions due to antisite disorder about 133 K [21,63] and (IV) a glassy behavior observed below at 80 K [21,63,64] owing to the coexistence of FM and AFM interactions. The bulk sintered in this paper showed only a strong high $T_c \approx 226$ K in the magnetization measurement, which evidences a predominance of a long-range ferromagnetic ordering. However, a careful analysis of the full width at half maximum (FWHM) of the stretching modes points out three different regions in FWHM with discontinuities near 135 K and 226 K, as observed in Fig. 3 (d) and (e). We can see those anomalies at the same temperatures in the linewidth of the SS and AS modes.

This result shows that, although the FC and ZFC magnetic curves do not evidence antisite disorder in LCMO, there is a new magnetic transition in LCMO, which can be characterized as an inhomogeneous magnetic phase [65]. This kind of change in phonon lifetimes was already observed as evidence of spin-phonon coupling [35,66]. This result is consistent with the existence of a majority ferromagnetic (FM) phase, basically an ordered region, and similar regions with disordered clusters, where the antiferromagnetic (AFM) interaction from Co$^{2+}$-O-Co$^{2+}$, Mn$^{4+}$-O-Mn$^{4+}$ and APB are predominate. This result
shows the power of Raman spectroscopy to indicate magnetic inhomogeneity via spin-phonon coupling in these perovskites. Even not observing this effect in the magnetization curve, we could detect it in Raman phonon parameters.

Finally, it is expected that the phonon renormalization due to the spin-phonon coupling depart of the measured position with relation to the expected position due only to the anharmonic temperature dependence, which is proportional to \( (M(T)/M_o)^2 \), where \( M(T) \) and \( M_o \) are the magnetization at temperatures \( T \) and 0 K, respectively, as predicted by the mean-field theory [67]. In Fig. 3(f), we showed that this model disagrees with the experimental data for temperatures down to 140 K, where the second transition is observed, clearly showing we have a new renormalization of the frequency at this transition that comes from the spin-phonon coupling. This unconventional behavior exhibited by LCMO can be associated with a competition between FM and AFM magnetic states promoted by the antisite disorder. Different values and signals of magnetic couplings \( J_{ij} \) can yield different contributions to the phonon renormalization induced by magnetic ordering. Interestingly, the SS mode renormalization in partially disordered LCMO was very similar to the one observed in \( Y_2\text{CoMnO}_6 \) (YCMO) [66], another multiferroic double perovskite whose stretching mode renormalization has been associated with the competition between FM and AFM magnetic states due to their frustrated Ising spin chain (E*-type) with \( \uparrow\uparrow\downarrow\downarrow \) spin pattern [68]. In both compounds (LCMO and YCMO), the different values of \( J_{ij} \) caused an SS softening behavior that has a dependence on the square of the temperature, as observed in Fig. 3(f).

4. Conclusion
Summarizing, in this paper, we showed that Raman spectroscopy is an efficient tool to detect low disorder levels in superexchange driven ferromagnetic double perovskites. By monitoring the spin-phonon coupling in LCMO ceramic obtained by temperature-dependent Raman spectra, we showed an anomaly at 135 K due to antiferromagnetic (AF) interactions in LCMO, which can be probed even when the disorder levels are low. At the same time, in magnetization measurements, only a single magnetic transition could be observed. This result presents Raman spectroscopy as a powerful tool to probe disorder in double perovskites.

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