Impact of Co/Mn cation ordering on phonon anomalies in La_2CoMnO_6 double perovskites: Raman spectroscopy

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Manifestation of Co/Mn ordering on the spin-lattice dynamics of La_2CoMnO_6 (LCMO) double perovskites is studied by Raman spectroscopy. We investigate the temperature dependence of the magnetic and the optical properties for (i) microcrystals containing both the ordered and disordered phases and (ii) Co/Mn ordered epitaxial films. Our results show distinct onsets of phonon mode softening in the vicinity of the magnetic phase transitions, revealing a strong spin-lattice coupling in LCMO. Moreover, Co/Mn ordering in the thin films leads to the appearance of additional excitations that had not been observed previously. We interpret these features as a result of Brillouin zone folding due to the doubling of the unit cell in the ordered phase.

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I. INTRODUCTION

Ferromagnetic insulators have recently received renewed interest due to their rich physics and potential novel applications.[1–5] They are potential candidates as multiferroics[1–3] because of the simultaneous occurrence of ferroelectricity and ferromagnetism leading to magnetodielectric coupling.[4,5] In this respect, the double-perovskite manganites with general formula A_2BMnO_6 (A=La, Bi; B=Co, Ni) are promising materials since they display ferromagnetic ordering and magnetodielectric coupling.[4–11]

The crystal structure and physical properties of bulk La_2CoMnO_6 (LCMO) have been studied extensively in the past,[6–11] showing that a well-ordered LCMO exhibits a monoclinic symmetry, while any deviation from it results into an orthorhombic phase similar to $LaMnO_3$. In the well-ordered LCMO phase, Co^{2+} and Mn^{4+} layers alternate, giving rise to a large local polarization as evidenced by the observed large dielectric constant.[5] However, in the disordered structure, the Co and Mn ions are randomly distributed at the B site and possess Co^{3+} and Mn^{3+} oxidation states. In the same fashion, oxygen nonstoichiometry in LCMO can also lead to a similar reduction of the oxidation state of B-site cations.[5–7] Of course, the magnetic properties of polycrystalline samples are definitely influenced by the presence of mixed ordered and disordered phases and/or oxygen vacancies. It has been found that, depending on the synthesis conditions, LCMO can have two ferromagnetic phase transitions at $T_{C2} \sim 150$ K and $T_{C1} \sim 220$ K.[6,7] The low-temperature magnetic transition temperature is usually related to the disordered structure.[6,7] Since the double-perovskite La_2CoMnO_6 presents significant magnetodielectric effect indicating a clear coupling between the lattice and the magnetic degrees of freedom,[5] it becomes interesting to correlate the role of its cation ordering and its magnetic properties.

Few efforts have been made to investigate the spin-lattice interaction of LCMO by Raman spectroscopy,[12] which is indeed a very sensitive and powerful tool to investigate the local and/or dynamical structural changes.[12–17] It has been extensively used to study the charge and/or orbital ordering and spin-lattice interactions in manganites and other related compounds.[12–17] In these cases, the impact of charge ordering is obvious as it doubles the size of the unit cell and lowers the symmetry of the crystal structure. These structural changes lead to the appearance of new phonon excitation in Raman spectra. However in the case of double-perovskite La_2CoMnO_6, the role played by the disordered and the ordered structures on the spin-lattice interaction remains unclear. In order to understand the influence of Co/Mn ordering on double-perovskite LCMO, we investigate the temperature dependence of phonon frequencies by Raman spectroscopy of two types of samples: (i) the microcrystals possessing both disordered and ordered LCMO phases and (ii) the well-ordered epitaxial thin films grown by pulsed-laser ablation. We confirm a spin-lattice coupling in both ordered and disordered phases as signaled by mode softening at the magnetic phase transitions. We also show that the Co/Mn ordering in thin films leads to additional phonon modes related likely to Brillouin-zone folding as a result of the doubling of the unit cell.

II. SAMPLES AND EXPERIMENTAL METHODS

Bulk La_2CoMnO_6 was synthesized using La_2O_3, CoO, and MnO_2 as the starting materials. First, the La_2O_3 were precalcined in air at 900 °C. Stoichiometric quantities of these oxides were then mixed, grinded, and put into an yttria-stabilized zirconia crucible, which was subjected to several heating cycles between 1000 and 1275 °C in air with several intermediate grindings to obtain a homogeneous mixture. In the final step, the resultant dark brown LCMO powder was pressed into pellets and annealed at 1300 °C in air for 25 h. The crystal structure of the resulting LCMO was confirmed to be orthorhombic with lattice parameters corresponding to a=5.45 Å, b=5.50 Å, and c=7.76 Å as characterized by powder x-ray diffraction at room temperature. The observed orthorhombic symmetry suggests that the obtained powder likely contains a partially disordered phase with a low-spin Co^{3+}/intermediate-spin Mn^{3+} configuration, which was further confirmed by the presence of two magnetic phase transitions at about 150 and 250 K (see below). The bulk sample roughly contains about 45% ordered phase as estimated from the magnetic data at 200 K.

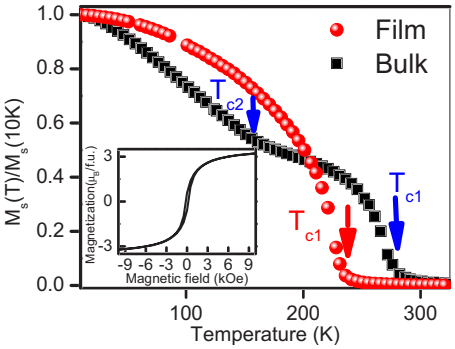

FIG. 1. (Color online) Normalized *M-T* curves of the bulk and film La_2CoMnO_6. The inset shows the **M-H** loop of the bulk sample recorded at 10 K.

Well-ordered epitaxial LCMO films on $SrTiO_3$ (100) were grown by pulsed-laser deposition at 800 °C in 600 mTorr O_2. Details of the growth conditions and structural and physical properties have been reported elsewhere.[5,9] Unlike our bulk-LCMO samples, these films with a thickness of 190 nm display a single magnetic transition around 240 K, which clearly demonstrates that they possess well-ordered *B* sites with only high-spin Co^{2+}/Mn^{4+} configuration. Out-of-plane lattice parameter of these films is found to be close to their bulk counterpart, indicating that they are partially relaxed.[9]

The Raman 0.5 cm^{-1} resolution spectra were measured in backscattering configuration using a Labram-800 microscope spectrometer equipped with a He:Ne laser (λ=6328 Å) and a nitrogen cooled charge coupled device (CCD) detector. To avoid sample heating, the power of the laser beam was kept below 0.3 mW using a 50× objective that focuses on a 3 μm diameter spot and allows the selection of microcrystals of the bulk samples with sizes larger than the laser spot size. Crystals were mounted on the cold finger of a Janis Research Supertran cryostat allowing for cooling rates from 2 to 8 K/min from 295 to 10 K.

Magnetization (M) as a function of temperature (*M-T* curves) and field (*M-H* loops) was measured with a Quantum Design superconducting quantum interference device magnetometer. *M-T* curves were recorded in the temperature range of 10–350 K. We measured the *M-H* hysteresis loops for applied magnetic fields in the range from −50 to 50 kOe at 10 K.

III. RESULTS AND DISCUSSION

A. Magnetic data

In order to establish the relation between the Raman modes and the magnetic phase transitions of La_2CoMnO_6 in both types of samples, we first measured their magnetization. For the epitaxial films, we observe only one *paramagnetic-to-ferromagnetic* phase transition around 240 K, as shown in Fig. 1 (see also Ref. 9). For the polycrystalline samples, this phase transition is still observed at around $T_{C1} \sim 250$ K followed by a second ferromagnetic transition T_{C2} at 150 K (Fig. 1). The paramagnetic inverse molar susceptibility of LCMO was also evaluated as a function of temperature (not shown), leading to a paramagnetic Weiss constant $\theta \sim 254\ \text{K} > T_{C2}$ which is characteristic of ferromagnetism as opposed to ferrimagnetism.[4] The inset of Fig. 1 shows a typical *M-H* hysteresis loop of the bulk-LCMO sample measured at 10 K. The *M-H* loop possesses a well-defined hysteresis with a very low coercive field of about 188 Oe. The narrow hysteresis loop indicates that disordered La_2CoMnO_6 is a soft magnetic material, making it also a potential candidate for spintronic applications.[7] We must emphasize here that well-ordered LCMO thin films with only Co^{2+}/Mn^{4+} ions show a relatively large coercive field (~3 kOe) in the case of our epitaxial films[9] due to the anisotropy imposed by the cationic ordering on LCMO. Films are also characterized by a 5.8 μ_B/f.u. saturation magnetization reaching the expected theoretical value of LCMO.[9] On the contrary, the saturation magnetization of the bulk sample was found to be only 3.66 μ_B/f.u. Insisting on the fact that bulk samples consist of both well-ordered and disordered phases, the observed low saturation magnetization is consistent with its structure and composition. Thus, it reveals that the bulk samples contain intermediate-spin Mn^{3+} and low-spin Co^{3+} ions and that the observed low temperature transition can be assigned to the ferromagnetic oxygen-deficient phase with T_{C2}=150 K.[6,7] In comparison, the epitaxial films are well ordered and consistent with Co^{2+}/Mn^{4+} ordering that favors ferromagnetic e_g^2-O-e_g^0 180° superexchange interaction in between Co^{2+} and Mn^{4+}.[6–9]

B. Raman data

From the magnetic measurements, we established a first impact of the structural ordering on transitions in the films and polycrystalline samples as a single magnetic transition was observed in the films. Here, we study both types of samples by Raman scattering as a function of temperature. We measured the Raman spectra of epitaxial films in the $x'x'$, xx, xy, and $x'y'$ polarization configurations. Typical Raman spectra showing the most noticeable features of a La_2CoMnO_6 microcrystal and an epitaxial film are compared in Fig. 2. Our results can also be compared directly to the recent theoretical predictions and experimental results on thin films for the monoclinic LCMO structure by Iliev *et al.*[12] Over the 24 allowed Raman modes, 9 modes were observed experimentally in films.[12] Our detailed study at room temperature shows that our microcrystals display 10 broad peaks at 99*, 156, 170*, 232*, 258, 283*, 483, 500, 630, and 645 cm^{-1}, while 12 are found at 103*, 150, 170*, 197*, 236*, 247, 281*, 422, 484, 498, 628, and 645 cm^{-1} for the epitaxial films. The asterisks denote the modes that were not experimentally observed in Ref. 12. It is also important to note that we did not observe the 408 cm^{-1} mode reported also in Ref. 12. Furthermore, the thin films displayed two additional modes compared to the bulk at 197 and 422 cm^{-1}. Finally, the Raman stretching mode frequencies of the films and crystals (e.g., 645 cm^{-1}) have very close values. This indicates that the films are partially relaxed for a thickness of about 190 nm.[8,9,12]

We must emphasize that the strong A_g mode at 645 cm^{-1} is also observed for the microcrystal Raman spectra. It is likely due to the monoclinic ordered phase that coexists in

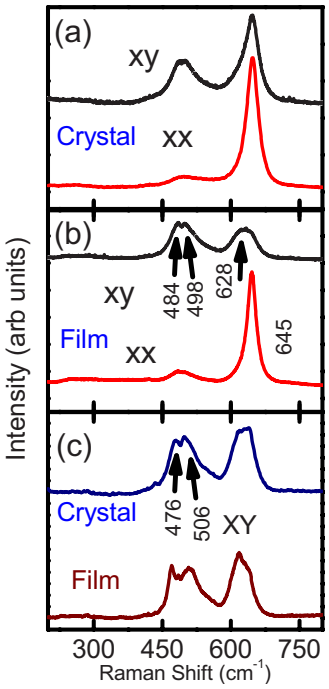

FIG. 2. (Color online) Raman spectra of (a) microcrystal and (b) epitaxial film recorded at 295 K in the *parallel-XX* and *crossed scattering-XY* configurations. (c) Raman spectra of the epitaxial film and micro crystal recorded at 10 K in crossed scattering-*XY* configurations.

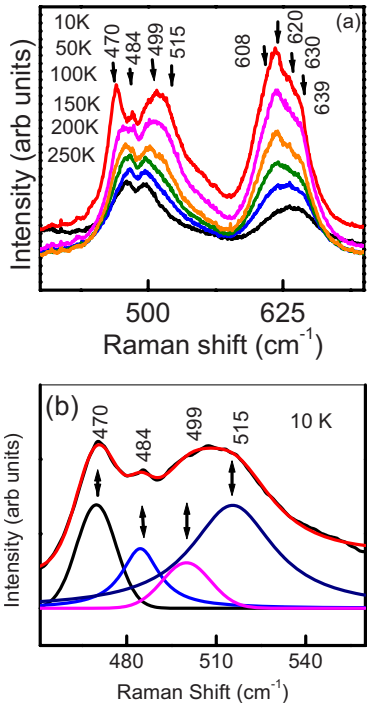

FIG. 3. (Color online) (a) Raman spectra of the epitaxial film recorded at different temperatures in the *crossed scattering-XY* scattering configurations. (b) A typical fit to the experimental 10 K curve displaying the four peaks.

the crystal with the LCMO-like disordered phase. This fact is further supported by the linewidth of the stretching mode at 645 cm^{-1}. For well-ordered films, the full width at half maximum is 23 cm^{-1}, whereas it is found to be 31 cm^{-1} for microcrystals. The apparent broadening in the case of the microcrystals is likely due to its disordered nature. Thus, these results illustrate the similarities and differences in the LCMO samples with various proportions of the ordered and disordered phases.

As one lowers the temperature of the microcrystals down to 10 K, the peaks at 483 cm^{-1} (FWHM: 34 cm^{-1}) observed at 295 K in the *xy* configuration show the softening and narrowing to 476 cm^{-1} (23 cm^{-1}), while the peaks at 500 cm^{-1} (74 cm^{-1}) display a hardening and narrowing to 506 cm^{-1} (53 cm^{-1}). In the case of the ordered epitaxial films, new peaks appear in the Raman spectra in the same *xy* configuration [see Figs. 2(c) and 3]. From the two modes at 483 cm^{-1} (34 cm^{-1}) and 498 cm^{-1} (55 cm^{-1}) observed at room temperature, two new modes emerge with decreasing temperature in Fig. 3(a). These four peaks at 10 K on a well-ordered LCMO sample can be fitted to extract their corresponding frequency (and FWHM) at 470 (18), 484 (15), 499 (19), and 515 cm^{-1} (34 cm^{-1}) as shown in Fig. 3(b). These features are neither observed in the case of our disordered micro-crystals nor were they observed in thin films by Iliev *et al.*[12]

As a simple scenario for the additional excitations observed in our ordered thin films with respect to previous reports,[12] one should consider the impact of substitution of B cations by B' in a simple perovskite as ABO_3 leading to $AB_{0.5}B'_{0.5}O_3$ stoichiometry. For a disordered substitution as in our bulk material and previous thin films,[12] phonon signatures should remain fairly similar to ABO_3 unless a structural change leads to a lower symmetry, new excitations, and different selection rules. In this case, the number of phonon excitations will be fairly similar to ABO_3 and should not agree fully with the theoretical predictions for the monoclinic phase of the ordered $A_2BB'O_6$ presented in Ref. 12. One expects that B/B' cation ordering with alternating layers of BO_6 and $B'O_6$ octahedra as in our ordered films will lead to additional excitations with respect to the disordered phase as a result of Brillouin-zone folding due to the doubling of the unit cell. Our data on our ordered thin films clearly show the presence of these predicted excitations not seen in previous films.[12] A close inspection of Figs. 2 and 3 also reveals that cation ordering splits, in general, single excitations of the disordered bulk into two peaks, reinforcing our scenario. These features in our thin films are indications that Co/Mn cation long-range structural order has been achieved with its major impact on the optical phonon spectrum.

Several Raman modes observed for the microcrystals and the thin films reveal a general softening trend, as reported for $RMnO_3$ compounds[13] and in LCMO.[12] Due to overlapping of Raman modes at 481 and 500 cm^{-1} with their newly observed neighbors, we could not precisely plot their frequency as a function of temperature. We have then focused on the 645 cm^{-1} phonon Raman shifts (Fig. 4) to evaluate the likely impact of Co/Mn ordering on the LCMO phase transitions. In Fig. 4(c), we show that the temperature dependence of the Raman mode around 645 cm^{-1} for the thin films correlates very well with the onset of magnetization at ~250 K. On the other hand, the same mode for the microcrystals shows a

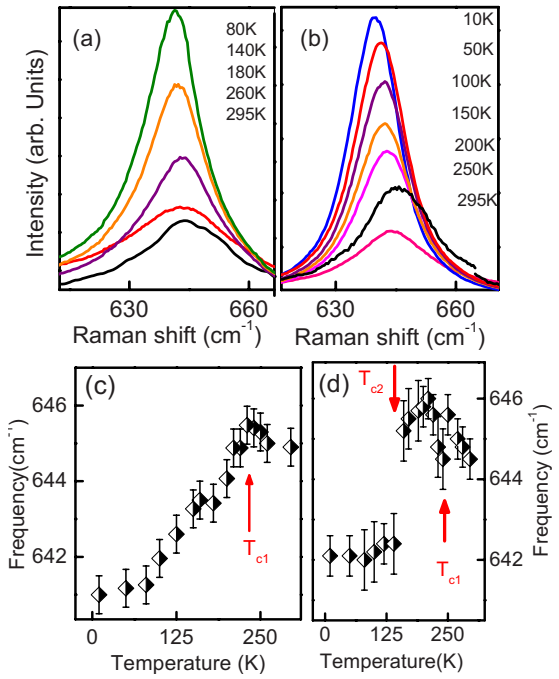

FIG. 4. (Color online) Raman spectra of (a) the epitaxial film and (b) the microcrystal recorded at different temperatures in the *parallel-XX* scattering configuration. Curves are presented in increasing temperature from top to bottom. (c) Temperature dependence relative shift in the stretching mode frequency on (c) thin film and (d) microcrystal.

clear and sharp discontinuity at 150 K corresponding to the lowest transition temperature [Figs. 1 and 4(d)]. The observed temperature dependence of the Raman modes in epitaxial films possesses two distinct characteristics that differentiate them from the microcrystals. First, the softening at 250 K is very prominent in the thin films and follows closely the magnetization (Fig. 1), while it is absent in the bulk.[9] Second, the ordered films display a very smooth softening down to 10 K without any anomaly at 150 K, whereas disordered microcrystals have only a sharp discontinuity at 150 K. This discontinuity might be the indication of a structural transition occurring in the disordered bulk which is totally absent for the ordered phase.

The coincidence of the softening and the magnetic transitions indicates a substantial spin-lattice interaction in this system. Similar effect was also observed in *A*-type AFM ordering in $R\mathrm{MnO}_3$ (R=La,Pr,Nd,Sm). Granado *et al.*[18] have interpreted such softening in terms of a spin-lattice (magnetoelastic) coupling caused by the phonon modulation of the exchange integral. However, the fact that all modes show general softening implies that phonons are isotropically renormalized by exchange integral and softening is not exclusive to 2D ferromagnetism like $R\mathrm{MnO}_3$ *A*-type order. Our observation of significant spin-lattice coupling at the transition also correlates well with the magnetodielectric effect measured on similar films that peaks just below the Curie temperature.[5] Obviously, the role of the ordered phase here could be to promote the coupling of the long-range electric polarization order (akin to the antiferroelectric) to the long-range ferromagnetic order parameter in the transition region.

IV. CONCLUSION

In summary, we have studied the temperature dependence of Raman and magnetic properties of La_2CoMnO_6 samples containing the *B*-site cation ordered and/or disordered phase. Our results display possible similarities and distinctions in the phonon anomalies and Raman shift discontinuities arising due to the cation disordering and/or ordering. Additional new peaks appear at low temperatures in the case of well-ordered films. They can be explained if one considers the doubling of the unit cell leading to Brillouin-zone and phonon branch folding. The observed differences in the Raman properties of these samples are well correlated with their magnetic properties. The ferromagnetic ordering below the Curie temperature produces a softening (redshift) of the Raman modes owing to a strong spin-lattice coupling in La_2CoMnO_6. These results may be easily generalized to understand the likely role played by the cation ordering in double perovskites.

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