Effects of Cation Vacancies in the Phonon Raman Spectra of LaMnO$_3$

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Raman spectra of La$_{1-x}$Mn$_{1-x}$O$_3$ ($x = 0, 0.01, 0.017, 0.022$, and 0.035) and La$_{0.91-\delta}Mn_{1-\delta}O_3$ polycrystalline samples, taken at $T = 10$ K and room temperature, are presented. All La$_{1-x}$Mn$_{1-x}$O$_3$ samples show at $T = 10$ K the presence of modes at about 480 and 610 cm^{-1}, including the rhombohedral and quasi-cubic orthorhombic samples. However, the Raman spectrum of the rhombohedral La$_{0.91-\delta}$Mn$_{1-\delta}$O$_3$ sample does not show these modes at $T = 10$ K, but presents weak and broad structures at $T = 295$ K. These results are discussed in terms of local structural distortions associated with Mn vacancies and/or carrier localization in manganese perovskites.

Introduction In recent years, much effort has been devoted to understand the physics involved in the transport and magnetic properties of the manganese perovskites. In addition to the double exchange (DE) model [1], the presence of carrier trapping mechanisms was invoked to explain the high resistivity of the paramagnetic (PM) phase [2]. The giant oxygen isotope T_C shift observed in La$_{0.7}$Ca$_{0.3}$MnO$_3$[3] suggests that lattice vibrations may play an important role in the electronic properties of these materials.

For perovskite-like materials, all the first-order Raman active vibrational modes are activated by deviations from the ideal cubic crystalline structure. As a consequence, defects and other extrinsic factors may strongly affect the observed Raman spectra. The Raman spectrum of the parent compound LaMnO$_{3.0}$ is dominated by two strong phononic peaks at ≈ 480 and ≈ 610 cm^{-1} [4 to 6]. We will refer to these modes as high frequency peaks (HFP). The low-T Raman spectrum of La$_{0.5}$Ca$_{0.5}$MnO$_3$ also shows the HFP [5]. Both compounds have D$_{2h}^{16}$ perovskite structure and show orbital ordering of the Mn^{3+} e$_g$ states, giving rise to a large cooperative Jahn-Teller distortion of the oxygen octahedra around the Mn^{3+} ions [7, 8]. On the other hand, low-T Raman spectra taken in fresh bulk surfaces of La$_{0.70}$Sr$_{0.30}$MnO$_3$ and Pr$_{0.62}$Sr$_{0.38}$MnO$_3$ single crystals, did not show the HFP [5]. These compounds are ferromagnetic (FM) with sharp FM–PM transitions at relatively high T_C values (366 and 304 K, respectively) [9], and do not present cooperative Jahn-Teller distortions of the oxygen octahedra [5]. Therefore, the presence of the HFP in the Raman spectra of manganese perovskites seems to be

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mainly associated with distortions of the oxygen octahedra. Recently, Abrashev et al. [10] reported that thin films of $La_{0.70}Ca_{0.30}MnO_3$ (T_C = 240 K) showed the HFP only for $T \geq T_C$. This result was interpreted as a manifestation of local distortions of the oxygen octahedra above T_C, and associated with Jahn-Teller polarons (JTP). These authors also observed the HFP in their rhombohedral samples of $LaMnO_{3+\delta}$, and ascribed them as JTP [11]. However, we reported that the low-T Raman spectrum of a rhombohedral $LaMnO_{3.1}$ ceramic sample did not show those peaks [5]. We should mention that the HFP are not allowed for perovskites with D_{3d}^6 space group [5, 11]. Therefore, we believe that it is important to elucidate this point.

It is well accepted that the excess of oxygen in $LaMnO_{3+\delta}$ cannot be accommodated interstitially in the lattice, and La and/or Mn vacancies must be present in these samples [12]. From a crystallographic point of view, the correct formula for these materials is $La_{1-x}Mn_{1-y}O_3$ with $x + y \approx 2\delta/3$. In this work, we study Raman spectra of $La_{1-x}Mn_{1-x}O_3$ ($x = 0, 0.01, 0.017, 0.022$, and 0.035) and $La_{0.91-\delta}Mn_{1-\delta}O_3$ polycrystalline samples, with orthorhombic and rhombohedral perovskite crystal structures.

Experimental Details   Details of sample growth and characterization of the $La_{1-x}Mn_{1-x}O_3$ samples were published elsewhere [13]. The $La_{0.91-\delta}Mn_{1-\delta}O_3$ sample was obtained following the nitrate decomposition route. Raw materials were La_2O_3 (99.999 %) and metallic Mn (99.99 %) and dissolved in nitric acid. Thereafter, the solution was heated until the solvent evaporated forming a powder that was annealed in air with intermediate grinding at 1173 and 1523 K for 24 and 6 h, respectively. The final synthesis temperature treatment was performed at 1523 K for 12 h in air. The room-T X-ray diffraction pattern of $La_{0.91-\delta}Mn_{1-\delta}O_3$ showed no evidence of spurious phases and is consistent with D_{3d}^6 perovskite structure. Magnetization measurements indicate that this sample is FM with $T_C = 243$ K, which is much higher than those of the FM $La_{1-x}Mn_{1-x}O_3$ Samples [13]. In the discussion below, we will assume that the $La_{0.91-\delta}Mn_{1-\delta}O_3$ sample presents only few Mn vacancies ($\delta \approx 0$). Details of the Raman experimental set-up were given previously [5]. The series of Raman measurements involving temperature variation were performed under an incident laser power density below ≈ 100 W/cm^2. For fixed-T measurements, the laser power density was kept below ≈ 500 W/cm^2.

Results and Discussion   Figure 1a shows the Raman spectra, at $T = 10$ K, for the $La_{1-x}Mn_{1-x}O_3$ samples with $x \leq 0.017$. As x increases one observes (i) a broadening of all the Raman modes, (ii) a systematic shift of the 290 cm^{-1} peak to lower frequencies, and (iii) a shift of the 604 cm^{-1} mode to higher frequencies. These effects are somewhat similar to those reported by others for the $La_{1-z}Sr_zMnO_3$ system with increasing z [6]. A study of the T-dependence of the frequency of the ≈ 610 cm^{-1} peak of these samples has been recently published [14]. The Raman spectra (at 10 K) of the FM samples ($La_{0.978}Mn_{0.978}O_3$, $La_{0.965}Mn_{0.965}O_3$, and $La_{0.91-\delta}Mn_{1-\delta}O_3$) are shown in Fig. 1b. A large difference between the Raman spectra of the $La_{0.91-\delta}Mn_{1-\delta}O_3$ sample and the other two FM samples is observed. The $La_{0.978}Mn_{0.978}O_3$ and $La_{0.965}Mn_{0.965}O_3$ samples show (i) the HFP, which are not observed in the $La_{0.91-\delta}Mn_{1-\delta}O_3$ sample, and (ii) a very small intensity at ≈ 430 cm^{-1}, corresponding to a narrow peak observed for $La_{0.91-\delta}Mn_{1-\delta}O_3$. We should mention that the intensity of the peak at ≈ 670 cm^{-1} of $La_{0.91-\delta}Mn_{1-\delta}O_3$ is highly dependent on the laser focused region of the sample.
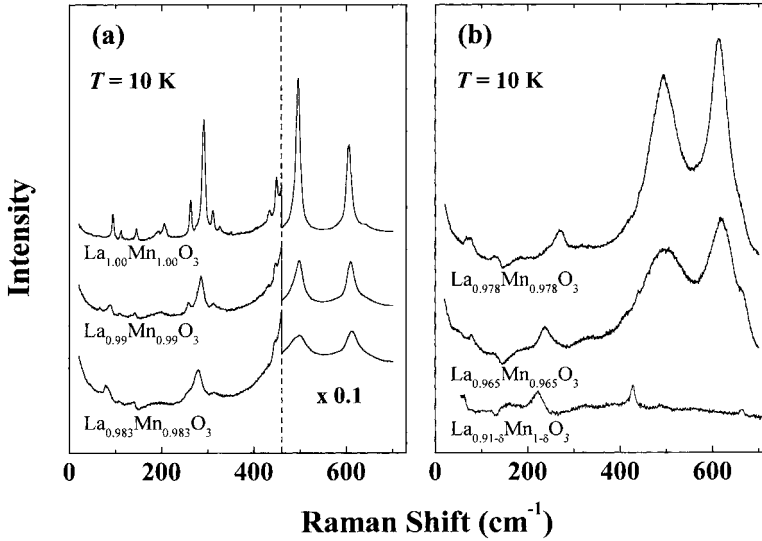
Fig. 1. Raman spectra, at $T = 10$ K, of the a) $La_{1-x}Mn_{1-x}O_3$ samples with $x = 0$, 0.01, and 0.017, and b) FM samples ($x = 0.022$ and 0.035, and $La_{0.91-\delta}Mn_{1-\delta}O_3$)

The T-dependence of the Raman spectra of the $La_{0.91-\delta}Mn_{1-\delta}O_3$ sample around the FM–PM transition is shown in Fig. 2. While the HFP are absent in the FM regime, these peaks are clearly observed at $T \gtrsim T_C$. This effect is similar to that observed for $La_{0.7}Ca_{0.3}MnO_3$ thin films [10], and the HFP at high temperatures may be ascribed to local distortions of oxygen octahedra associated with the carrier localization in the PM regime.

Figure 3 shows the Raman spectra of the rhombohedral samples, $La_{0.965}Mn_{0.965}O_3$ (R1) and $La_{0.91-\delta}Mn_{1-\delta}O_3$ (R2), at room temperature. Although the HFP are present in both samples, these peaks are consider-ably stronger in the R1 sample. At this temperature both samples are PM insula-tors with comparable Mn^{3+}/Mn^{4+} ratio, therefore, local distortions due to carrier localization are not sufficient to under-stand the higher intensity of the HFP in the R1 sample. On the other hand, the number of Mn vacancies in the R1 sample is supposed to be much higher than in the
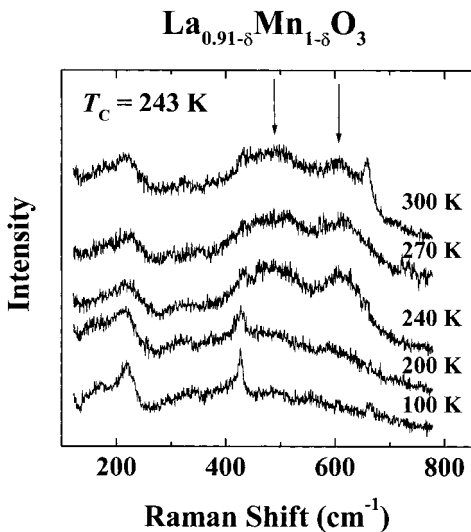

Fig. 2. T-dependence of the Raman spectrum of the $La_{0.91-\delta}Mn_{1-\delta}O_3$ rhombohedral sample ($T_C = 243$ K)

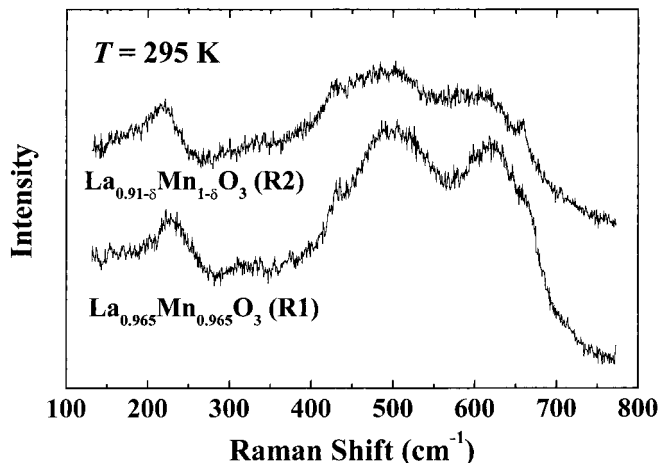Fig. 3. Raman spectra, at $T = 295$ K, of the rhombohedral samples $La_{0.965}Mn_{0.965}MnO_3$ (R1) and $La_{0.91-\delta}Mn_{1-\delta}O_3$ (R2)

R2 sample. These Mn vacancies may produce local static distortions of the oxygen octahedra, and be responsible for the enhanced intensity of the HFP in the Raman spectrum of rhombohedral Mn-deficient samples. Notice that, in addition to the ionic binding, the Mn and O ions have a considerable covalency, in contrast to La and O. Hence, Mn vacancies are expected to cause stronger distortions of the oxygen octahedra than the La vacancies.

Conclusion In summary, Raman scattering measurements were performed in $La_{1-x}Mn_{1-y}O_3$ ceramic samples. Our results suggest that the presence of the HFP in rhombohedral and quasi-cubic orthorhombic samples are associated with local distortions of the oxygen octahedra, caused by Mn vacancies throughout the samples and/or by carrier localization.

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