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Raman Study of the Variations of the Jahn-Teller Distortions through the Metal–Insulator Transition in Magnetoresistive $La_{0.7}Ca_{0.3}MnO_3$ Thin Films

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The polarized Raman spectra of $La_{0.7}Ca_{0.3}MnO_3$ magnetoresistive thin films deposited on $LaAlO_3$, $SrTiO_3$, YSZ, and MgO substrates were studied in a broad temperature range including T_c. Depending on variations of their intensity and linewidth upon cooling, the Raman bands could be classified into two groups. The lines corresponding to Raman allowed modes of the rhombohedral (or orthorhombic) structure grow in intensity and become narrower at low temperatures. In contrast, the broad Raman bands centered near 470, 485 and 610 cm^{-1} strongly decrease in intensity below T_c and display a correlation to the resistivity of the sample. We argue that these bands correspond to lattice vibrations activated by the dynamic Jahn-Teller distortions and by presence of small polarons around the Mn^{3+} sites. The correlation between polaron lifetimes and phonon linewidth is also discussed.

The discovery of large negative magnetoresistance (the so-called "colossal magnetoresistance", CMR) near the temperature of the coincident insulator–metal and paramagnetic (PM)–ferromagnetic (FM) transitions in perovskite-like $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba, Pb) generated a renewed interest in these materials [1]. The electronic and magnetic properties of these compounds were found to be very sensitive to small changes of the crystallographic structure. Generally, the perovskite distortions can be divided into two groups: distortions changing Mn–O–Mn bond angles governed by the tolerance factor $t = (r_R + r_O)/(r_{Mn} + r_O)\sqrt{2}$, and distortions changing the Mn–O distances governed by the magnitude and the spatial coherence of the Jahn-Teller distortions of the $Mn^{3+}O_6^{2-}$ octahedra. Almost all of the compounds exhibiting CMR have either orthorhombic (Pnma) or rhombohedral ($R\bar{3}c$) static (coherent) distortions as well as dynamical (incoherent) distortions of the MnO_6 octahedra. The Raman spectroscopy is a powerful tool for investigation of these distortions since there are no Raman-active

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lattice vibrations in the ideal cubic $Pm\bar{3}m$ perovskite and, therefore, all phonon features in the spectra originate from either coherent or incoherent lattice distortions.

The Raman spectra of the orthorhombic and the rhombohedral phases of the parent $LaMnO_3$ compound were studied previously [2,3]. It was established for the rhombohedral phase that the angle of the long-range coherent static tilt of MnO_6 octahedra is proportional to the frequency of the "soft" A_{1g} mode, whereas the strong broad lines in the 450 to 600 cm^{-1} range were assigned to vibrations activated by the dynamic Jahn-Teller distortions. Here we report the polarization and temperature dependence of the Raman spectra of doped $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) thin films deposited on different substrates.

The preparation of the films deposited on four different substrates ($LaAlO_3$, $SrTiO_3$, YSZ, and MgO, respectively) using off-axis radio frequency magnetron sputtering was described elsewhere [4]. The Raman spectra were obtained in a backward scattering configuration using a single spectrometer LABRAM, equipped with microscope, charge-coupled-device detector and appropriate notch filter. The 632.8 nm He–Ne laser line was used for excitation. For the low-temperature measurements the samples were mounted on the cold finger in a He-gas-flow cryostat. At room temperature the Raman spectra of all samples are dominated by three broad bands centered near 230, 480, and 610 cm^{-1}, respectively (see Figs. 1, 2 and 3). The comparison of the polarized Raman spectra shows that the films on $LaAlO_3$ and $SrTiO_3$ are single-crystalline, whereas the ones on YSZ and MgO substrates are polycrystalline (for the latter two samples the Raman spectra are insensitive to the orientation of the polarization of the incident light, e_i, with respect to the crystallographic directions of the substrate). This is consistent with the X-ray diffraction data [4] and the fact that the lattice mismatch film–substrate increases from 1.8% for the LCMO/$LaAlO_3$ to 9.0% for the LCMO/MgO system.

The three broad lines at 230, 480 and 610 cm^{-1} dominating the spectra have been previously assigned rather controversially to: (i) quasi-cubic F_{1u} infrared-active modes, activated by local distortions [5]; (ii) second-order Raman scattering [6,7]; (iii) Raman-allowed modes of the orthorhombic Pnma structure [8]. Based on the similarity of the LCMO spectra with those of rhombohedrally distorted $LaMnO_3$ [3], it is more plausible, however, to assign the line near 230 cm^{-1} to oxygen vibrations originating from the librational (rotation-like) motion of the MnO_6 octahedra. Such an assignment is consistent with the large oxygen isotope shift [8] and the strong dependence of the frequency on the temperature and A-site substitutions [6,7]. Concerning the broad lines near 470, 485 and 610 cm^{-1}, as previously proposed [3], their appearance in the Raman spectra can be ascribed to incoherent Jahn-Teller distortions of MnO_6 octahedra. Indeed, these lines have been observed in the Raman spectra of both orthorhombic and rhombohedral samples [3, 5 to 7] and, therefore, they are not sensitive to the long-range ordering of the MnO_6 octahedra.

In the case of LCMO films deposited on $LaAlO_3$ and YSZ it was possible to perform precise measurements of the variations of the Raman spectra with temperature.[2]) It was found that the intensity of the Jahn-Teller-distortion induced lines near 470, 485

[2]) For the other samples due to the defocusing by the cryostat window of the confocal laser beam, in the Raman spectra strong signals originating from the substrates were observed (see bottom panel of Fig. 2).

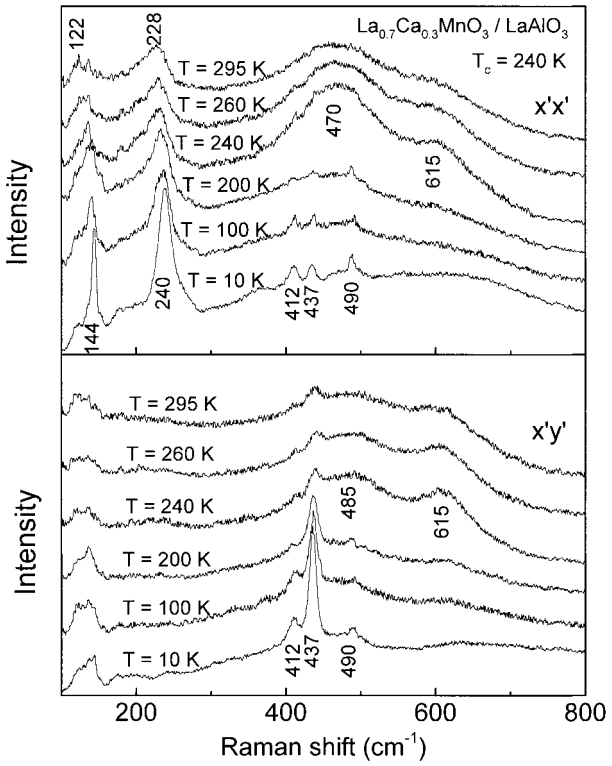

Fig. 1. Polarized Raman spectra at different temperatures of an oriented $La_{0.7}Ca_{0.3}MnO_3$ film ($T_c = 240$ K) deposited on $LaAlO_3$. The scattering configurations are indicated on the spectra. The feature at 122 to 144 cm^{-1} is due to a leakage from the $LaAlO_3$ substrate

and 610 cm^{-1} depends strongly on the resistivity of the sample. Fig. 1 shows the variation with temperature of the $x'x'$ and $x'y'$ Raman spectra (x, y, x' and y' are the quasi-cubic [100], [010], [110], and [1$\bar{1}$0] directions, respectively) of a high-quality LCMO/$LaAlO_3$ film with $T_c = 240$ K and low-resistive FM state at low temperatures. With lowering temperature the intensity of the lines near 470, 485 and 610 cm^{-1} increases, reaching a maximum near T_c and then abruptly decreases in the metallic state. In contrast, for the polycrystalline LCMO/YSZ film with $T_c = 190$ K and a high-resistive low temperature FM state the intensity of the same lines continuously increases with lowering temperature down to 10 K (Fig. 2). Therefore, the intensity of these three bands and, hence, the degree of the Jahn-Teller distortions correlates with the resistivity of the sample but not with the FM ordering, in consistence with the results of Bilinge et al. [9].

The width of the lines near 470, 485 and 610 cm^{-1} exhibits a pronounced minimum at T_c (see the inset in Fig. 3). To explain this minimum it is plausible to assume that the mean phonon lifetime, which governs the phonon linewidth, depends on mainly two factors: the time of anharmonic lattice relaxation τ_{anh} determined by the decay of the corresponding phonon into pairs of phonons with opposite momenta, and the mean lifetime τ_{pol} of the Jahn-Teller polaron at the Mn^{3+} site. The temperature dependence of the linewidth in this case will be given by the expression:

$$\Gamma = 2/c(1/\tau_{anh} + 1/\tau_{pol})\,. \tag{1}$$

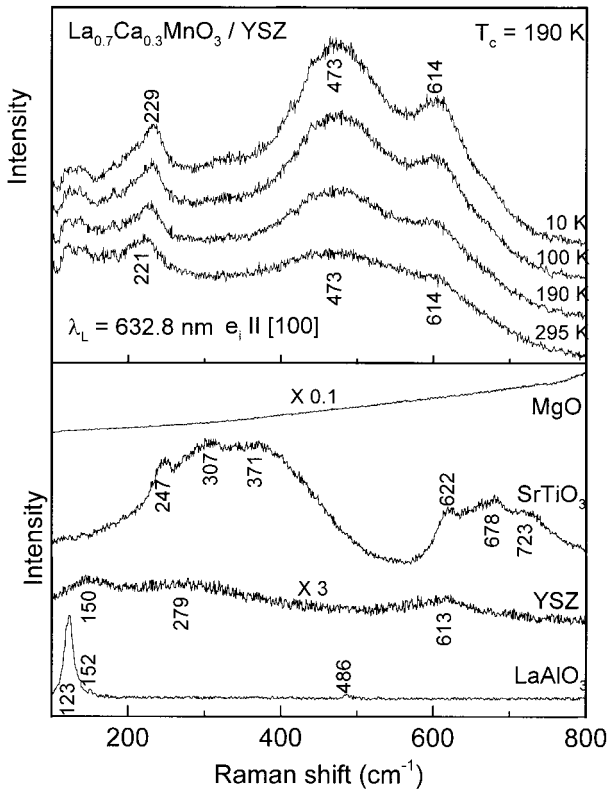

Fig. 2. Raman spectra at different temperatures of a polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ film with $T_c = 190\,K$ deposited on YSZ (top panel). Raman spectra at room temperature of the different substrates (bottom panel). The polarization of incident laser light is along quasi-cubic [100] direction. No analyzer has been used

The small polarons are well defined quasiparticles for $\tau_{pol} \gg \tau_{anh}$, and the phonon bands in this case should be well resolved in the Raman spectra around and above T_c. At temperatures well below T_c, due to the increased mobility of the charge carriers, τ_{pol} becomes comparable to or smaller than τ_{anh}, which means that the quasistatic distortion cannot develop around the Mn^{3+} sites during the phonon lifetime. Correspondingly, the Raman lines originating from the Jahn-Teller distortions disappear. To estimate τ_{pol} quantitatively we used the formula describing the dc resistivity in the model of hopping small polarons:

$$\varrho \propto \frac{\tau_{pol} k_B T}{ena^2}\,, \tag{2}$$

where n is the concentration of the polarons taken as $(1-x)/a^3$, where x and a are the doping and the hopping distance assumed to be equal to the Mn–Mn distance, respectively. It is evident from equation (2) that $1/\tau_{pol}$ scales as T/R, where R is the resistance of the film. Thus one can rewrite equation (1) in the form:

$$\Gamma(T) = \Gamma_0(1 + n(\omega/2)) + AT/R\,, \tag{3}$$

where $n(\omega/2)$ is the Bose factor.

The last expression was fitted to the experimentally measured linewidth and resistance R in the temperature range between 150 and 300 K, adjusting the parameters Γ_0 and A. The estimated value of 6.7 ps for the maximum polaronic lifetime τ_{pol} near T_c is

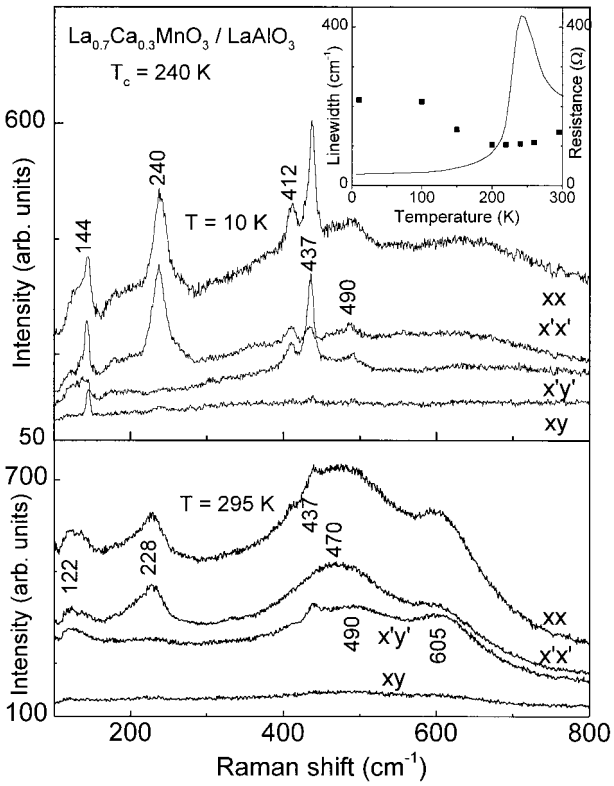

Fig. 3. Polarized Raman spectra at 10 K (top panel) and 295 K (bottom panel) of an oriented $La_{0.7}Ca_{0.3}MnO_3$ film ($T_c = 240$ K) deposited on $LaAlO_3$. The scattering configurations are indicated on the spectra. The feature at 122 to 144 cm^{-1} is due to a leakage from the $LaAlO_3$ substrate. The inset shows the temperature dependences of the film resistance (full line) and the width of the line near 610 cm^{-1} (squares)

in good agreement with the resistivity data. Indeed, substituting τ_{pol} in equation (2) one obtains $\varrho(T_c) = 1.9 \times 10^{-4}$ Ωm. On the other hand, the resistivity of the films under study may be estimated using the relation $\varrho \propto Rd$ where d is the film thickness, and the proportionality coefficient depends on the exact geometry of the resistivity measurement. In our case $d = 400$ nm and $R = 430\,\Omega$ at T_c, which gives $\varrho(T_c) = 1.7 \times 10^{-4}$ Ωm, a value surprisingly close to the one obtained from the Raman spectra.

It follows from Figs. 1 and 3 that for the samples exhibiting metallic behavior at low T, the Raman spectra are characterized by a significant narrowing of the line near 230 cm^{-1} below T_c and the appearance of new narrow lines in the 400 to 500 cm^{-1} region. The strong narrowing of the 230 cm^{-1} line has been reported earlier by Podobedov et al. [7] and attributed to the spin–lattice interaction in the spin-ordered FM phase. A more reasonable explanation of the narrowing, however, could be the increasing of long-range structural coherence due to the reduction of the dynamic Jahn-Teller distortions as was proposed by Irwin et al. [8].

Using a simple model we will further show that the intensity of each particular line in the Raman spectra of these compounds is related to mainly one type of distortion. Indeed, the orthorhombic Pnma structure (with Glazer's notations ($a^-b^+a^-$) [10]) of $LaMnO_3$ can be represented as a superposition of three independent distortions acting on the ideal cubic $Pm\bar{3}m$ perovskite. Two of these are rotations around [010] and [101] directions, each rotation alone resulting in a relatively simple space group: P4/mbm

[$(a^0a^0b^+)$, $\sqrt{2}a_p \times \sqrt{2}a_p \times a_p$] or Imma [$(a^-a^-b^0)$, $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$], respectively, with relatively small number of Raman-active modes. The third distortion is of Jahn-Teller type which if ordered leads to a P4/mbm space group. With a few exceptions, each Raman-active mode in the real orthorhombic Pnma structure has a counterpart in only one of these three simpler structures. Therefore, the increase in intensity of a given phonon line can directly be related to the increase of one of the three basic distortions. For example, the most intensive line with B_{2g} symmetry near 610 cm^{-1} in $RMnO_3$ (R = Y, La) [2] is unambiguously connected to the presence of Jahn-Teller distortions.

This model, however, cannot explain the appearance of the three narrow lines in the 400 to 500 cm^{-1} range at low temperatures in low-resistive samples. The experimentally established polarization properties of the 437 cm^{-1} line are incompatible with those expected for a rhombohedral E_g mode [3]. No reasonable correspondence could also be established with the well known Raman modes of the insulating orthorhombic $RMnO_3$ (R = Y, La) [2]. Therefore, the origin of the low temperature Raman lines of $La_{1-x}A_xMnO_3$ in the 400 to 500 cm^{-1} range remains unclear, indicating that an assignment to electronic or spin excitations existing in the metallic-state phase cannot be excluded.

In conclusion, the observation of significant changes in the Raman spectra of $La_{0.7}Ca_{0.3}MnO_3$ through the metal–insulator transition provides evidence for a strong reduction of the Jahn-Teller distortions in the metallic phase. The analysis of the temperature dependence of the linewidth of the Raman lines related to the Jahn-Teller distortions allows to estimate the value of the polaron mean lifetime near T_c, which is in good agreement with the resistivity data. A model connecting the appearance of some lines in Raman spectra with the presence of a definite type of lattice distortions is proposed.

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