Micro-Raman evidence for topological charge order across the superconducting dome of La$_{2-x}$Sr$_x$CuO$_4$ 

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The doping dependence of the micro-Raman spectra of high quality La$_{2-x}$Sr$_x$CuO$_4$ microcrystals with $x=0.0-0.45$ has been investigated in the region 10-300 K. The phonon at $\sim$100 cm$^{-1}$ of the orthorhombic phase shows a classical soft mode behavior up to $x=0.17$, supporting its correlation with the LTO to HTT transition. In the xx/yy polarization spectra of the superconducting concentrations new modes at $\sim$150 and 370 cm$^{-1}$ related to the symmetry breaking and a broad band at $\sim$280 cm$^{-1}$ are attributed to the charge ordering at temperatures well above $T_c$. At all temperatures studied a correlation has been found between the doping dependence of the transition temperature and the intensity of the bands at $\sim$150, $\sim$280, $\sim$370 cm$^{-1}$, the intensity of the La/Sr mode, and the asymmetry of the apex phonon.

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INTRODUCTION

It is known that the La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) superconductor shows a variety of phases with doping and temperature \[1\]. One of the main conclusions from the Raman investigations of the vibrational modes of La$_2$CuO$_4$ has been the existence of a soft mode at $\sim$100 cm$^{-1}$ (12 meV) of $A_g$ symmetry, attributed to tilting vibrations of the CuO$_6$ octahedra about the diagonal (110) axis \[2, 3, 4\]. This mode has been correlated with the observed High Temperature Tetragonal (HTT) to Low Temperature Orthorhombic (LTO) structural phase transition of LSCO \[5\] and has been studied for Sr doped samples \[6\]. In this work we have investigated the doping dependence of the micro-Raman spectra \[1\] of La$_{2-x}$Sr$_x$CuO$_4$ microcrystals with Sr doping in the range 0.00 $\leq$ $x$ $\leq$ 0.45 having been characterized as described elsewhere \[6\]. The Raman spectra were obtained in the 10-300 K temperature region. The carefully prepared samples have been characterized as described elsewhere \[6\]. The Raman spectra were obtained in the 10-300 K temperature region. The carefully prepared samples have been characterized as described elsewhere \[6\]. The Raman spectra were obtained in the 10-300 K temperature region. The carefully prepared samples have been characterized as described elsewhere \[6\]. The Raman spectra were obtained in the 10-300 K temperature region. The carefully prepared samples have been characterized as described elsewhere \[6\].

EXPERIMENTAL SETUP

Individual microcrystallites from a selected series of high quality La$_{2-x}$Sr$_x$CuO$_4$ polycrystalline compounds, with Sr doping in the range 0.00 $\leq$ $x$ $\leq$ 0.45 have been studied in the 10-300 K temperature region. The carefully prepared samples have been characterized as described elsewhere \[6\]. The Raman spectra were obtained in the approximate y(zz)$\bar{y}$ and y(xx)$\bar{y}$ (or x(yy)$\bar{x}$) scattering configurations or a mixture of them (as the x and y axis could not be discriminated in the twinned samples) at nominal temperatures from 10K to RT with a Jobin-Yvon T64000 triple spectrometer, equipped with a liquid nitro-
gen cooled CCD and a microscope (×100 magnification). Low temperatures were achieved by using an open cycle Oxford cryostat operating with liquid nitrogen or with liquid helium. The 514.5 nm of an Ar+ laser was used for excitation at a power level of ≤0.1 mW/µm². The local sample heating due to the laser beam was estimated to be less than 10 K. Accumulation times were of the order of 4-5 hours and usually two microcrystallites have been studied for each Strontium concentration (i.e. x = 0.00, 0.03, 0.05, 0.07, 0.092, 0.125, 0.17, 0.20, and 0.24).

RESULTS

Typical spectra for selected doping and temperatures in the y(zz)g and y(xx)g (or x(yy)g) polarization, are shown in Figures 1 and 2, respectively. In all cases, the two strong La/Sr and apex oxygen phonons of A_g symmetry appear. According to the La2−xSrxCuO4 phase diagram, the structural critical transition temperature, T_{ot}, for the insulating La_{1.97}Sr_{0.03}CuO4 sample is ~560K [1]. Thus, this compound remains orthorhombic throughout the temperature range studied and the soft mode appears in the low energy part of the zz polarization spectra for all temperatures (Fig.1a). The mode at ~270 cm⁻¹ attributed to the vibrations of the plane oxygens along the c axis is observed in all zz spectra of Fig.1a. This phonon is also correlated with the HTT→LTO structural phase transition since the vibrations of the plane oxygens are not Raman active in the tetragonal phase [2, 3, 12]. Concerning the xx/yy polarization spectra for the x=0.03 sample (Fig.2a), new bands at ~150 and 370 cm⁻¹ are observed for temperatures below ~100 K. These broad peaks are weakly observed at the same low temperatures in the zz polarization spectra (Fig.1a). With increasing doping these two bands appear at much higher temperatures, even at RT in the spectra of the superconducting materials (tetragonal phase, Fig.2b-2e). Therefore, their appearance cannot be related with the HTT→LTO structural phase transition. Besides, a weak mode at ~100 cm⁻¹ rapidly softening with increasing temperature (Fig.2a) is apparently an escape from the zz polarization.

In the zz polarization spectra of the underdoped superconductor La_{1.908}Sr_{0.092}CuO4 with T_{ot} ~300K, the modes at ~100 and 270 cm⁻¹ are observed only below 250 K (Fig.1b). For T>250 K they are not detectable due to the small tilting of the octahedra, in agreement with their relation to the orthorhombic deformation of the cell. The weak peaks at ~150 cm⁻¹ and ~365 cm⁻¹ must be the same modes with the xx/yy polarization spectra (see Fig.2b). The very broad band at ~280 cm⁻¹ observed in xx/yy polarization at low temperatures with increasing intensity should not be confused with the narrow peak at ~270 cm⁻¹ of the plane oxygens that appears in the zz polarization spectra. The intensity increment of the three bands at ~150, ~280, and ~370 cm⁻¹ with decreasing temperature becomes more obvious in the samples with x=0.125 and 0.17 (Fig.2c,d). In La_{1.76}Sr_{0.24}CuO4 the intensity of the three broad bands appears substantially reduced (Fig.2e). This indicates a doping dependence of these bands and, possibly small lattice distortions induced by the variation of the Sr content. The dependence of these bands on temperature and Sr concentration is examined below.

For the x=0.125 compound, some traces of the soft mode can be detected in the zz spectrum at 250 K with increasing intensity at lower temperatures (Fig.1c). Concerning the x=0.17 sample the soft mode start appearing in the zz spectra at even lower temperatures (Fig.1d), in agreement with the phase diagram, where no tilting is expected in the tetragonal phase above 150 K [1]. The soft mode has not been detected in the zz spectra for any temperature in the overdoped superconductor La_{1.76}Sr_{0.24}CuO4 (Fig.1e) and for x=0.20 as expected, since the compound remains tetragonal at any temperature [1].

The soft mode behavior of the low energy A_g mode at ~100 cm⁻¹ has already been shown for low Sr concentrations, up to x=0.07 [2, 3, 4]. In Figure 3a the temperature dependence of the energy of this mode for selected concentrations is presented. The values of the energy were determined by fitting the low energy part of the Raman spectra with Lorentzian curves. In Fig.3a, the continuous lines are best fit to the data with curves ω_{soft} ∝ (T_{ot} - T)^{1/2}, which assume a 2nd order phase transition. For most concentrations the zero phonon energy occurs close to the structural critical temperature of each concentration. But, for the x=0.17 sample, the soft mode energy tends to zero at temperature fairly larger than T_{ot}. This discrepancy may originate from the fact that the soft mode peak for this sample is very weak for all temperatures studied, and, therefore, the accurate determination of the energy was very difficult. Figure 3b shows the temperature dependence of the linewidth of the soft mode, for the x=0.092-0.17 samples. In each case, on approaching the T_{ot} the width increases as in a second order phase transition. Also, it should be noticed that, the soft mode is very weak for temperatures above 200 K, for the x=0.092, 0.125, and 0.17 samples (Fig.1b, c, d), and, therefore, the fitting results above this temperature are not taken into account in graphs of Fig.3. The above results support the correlation of this mode with the structural phase transition HTT→LTO. As seen in Fig.4, the energy of the soft mode decreases with increasing Sr content while its width increases as expected from the reduced tilting of the octahedra with increasing doping.

As mentioned, the mode at ~270 cm⁻¹ observed in the zz scattering polarization is attributed to the vibrations of the plane oxygens along the c axis of A_g symmetry. It
is correlated with the structural phase transition, since it appears only in the spectra of the orthorhombic phase of the compound, just like the soft mode. In particular, for the insulating samples (Fig.1a for x=0.03) this mode appears in the whole temperature range 10-300 K, while, for the doped x=0.092 and 0.125 samples it can only be seen at temperatures below 250 K. For the optimally doped x=0.17 sample, the appearance of this mode at temperatures above 150 K (which is the nominal T_{ot} for this compound), just like the soft mode, supports the assumption of the existence of tilted octahedra at this concentration and, thus, the T_{ot} for this sample should be considered \sim\sim 200 K. For the overdoped samples this mode has not been detected in all temperatures studied. Although the weakness of this mode and the existence of the strong La/Sr phonon close to it make difficult the accurate determination of the mode energy and width, it can be clearly seen that there is an almost linear increase in energy with decreasing temperature of the order \sim 5-6 \text{ cm}^{-1} (Fig.1). This result is in disagreement with previously reported data where no energy shift with temperature has been observed for this mode \[2,3\]. In addition, it should be clarified that, although the appearance of this mode is correlated with the LTO\rightarrow HTT transition, it does not show a classical soft mode behavior, i.e., its energy does not tend to zero near T_{ot} and its width does not show a significant broadening, similar to the broadening of the mode at \sim 100 \text{ cm}^{-1}.

In Figure 5a the variation of the energy of the La/Sr mode as a function of temperature for the x=0.092-0.24 superconducting samples is presented. As seen, the phonon energy decreases almost linearly with temperature for each Sr content by approximately 3-4 \text{ cm}^{-1} in the range 10-300 K. A similar behavior has also been detected for the insulating x=0.0, x=0.03 (also shown in Fig.5a) and underdoped superconducting (x=0.05, 0.07) compounds \[3\]. On the contrary, the apex energy remains practically constant with temperature for all compounds in the x=0.0-0.17 range (Fig.5b and Ref. \[3\]). Instead, there is a decrease of approximately 3 \text{ cm}^{-1}, with increasing temperature for the overdoped (x=0.24) compound. It should be marked that for the optimally doped compounds (x=0.125 and 0.17), the material undergoes a structural phase transition HTT\rightarrow LTO phase in the temperature range studied. This transition is correlated with the tilting of the CuO_6 octahedra about the (110) axis and apparently it does not affect the energy of the apex oxygen.

Figure 6 shows the linewidths of the La/Sr and apex oxygen modes with varying temperature for several doping levels. For all Sr concentrations the linewidth of both modes shows a typical anharmonic behavior increasing almost linearly with temperature above 70 K. The total width increment is about 8 \text{ cm}^{-1}, for both phonons in all concentrations. The relative intensity of the two modes as a function of temperature is presented in Fig.7 for the same concentrations. In a first approximation the relative intensity increases with temperature for all concentrations studied. But it appears that in the temperature range \sim 150-250 K there are some profound deviations from linearity for the samples around optimal doping. The maximum deviation is for the x=0.125 compound, it is reduced for x=0.17 and it seems gradually to disappear for x=0.092, and x=0.24. Since no structural modifications are expected at low temperatures for these compounds, this change perhaps involves other mechanisms and it is probably related with the plateau in the doping dependence of T_c and the charge ordering [10]. It is also clear that the correlation observed at RT between this relative intensity and the variation of T_c with doping [6] remains at low temperatures.

Figure 8 shows the temperature dependence of the average energy and total apparent width of the wide band at \sim 150 \text{ cm}^{-1}. At room temperature there is a band energy difference among the various concentrations, which diminishes at low temperatures. Besides, the temperature dependence of the band energy depends on the amount of doping. The bandwidth is almost independent of temperature for x\geq 0.20, while for lower doping levels it increases with decreasing temperature (Fig.8). One can observe in Figure 2 that this band for certain concentrations and below some temperature splits in two or three modes. Therefore, the modifications shown in Fig.8 actually represent changes in the relative intensity and the width of those modes.

Figure 9 shows the temperature dependence of the energy and width of the symmetry forbidden mode at \sim 370 \text{ cm}^{-1}. For the x=0.092-0.24 compounds the energy and the width of the mode seems to be independent of doping and temperature. In the insulating sample (x=0.03) a mode of similar energy appears in the xx/yy spectra for temperatures below 100 K (Fig.2a). The energy of this mode depends strongly on temperature decreasing by \sim 8 \text{ cm}^{-1} from T=90 to 10 K. Its linewidth is initially narrow, but with decreasing temperature it increases reaching at 10 K almost the same value as for the x=0.092-0.24 samples (Fig.9b).

The broad band at \sim 280 \text{ cm}^{-1} appears mainly in the low temperature xx/yy spectra. At room temperature, traces of this band have been detected only for the x=0.17 sample (Fig.2d). For x=0.092 and 0.125 the band is observed for temperatures below 250 K (Figs.2b and 2c), while, for the x=0.03 sample it seems not to be present to the lowest temperatures studied (Fig.2a). Similar to the \sim 150 and 370 \text{ cm}^{-1} broad peaks, the appearance of this band cannot be correlated with Raman active modes or the HTT\rightarrow LTO phase transition. For x=0.125 the transition temperature T_{ot} is nearly the same with the temperature at which the \sim 280 \text{ cm}^{-1} band appears, but this is not the case for the x=0.092 and x=0.17 samples. Besides, the x=0.03, which is orthorhombic even at room temperature does not show this broad band. For the x=0.092-0.17 compounds, the energy of this band does not vary with temperature within experimental error (Fig.10a), while its width appears to be very large (\sim 100 \text{ cm}^{-1}) and almost independent of temperature for
all samples (Fig.10b).

**DISCUSSION**

The apex phonon energy shown in Fig.5 (and from Ref.[8]) remains practically unaffected with the variation of temperature for the x=0.03-0.17 samples and, only, for the overdoped x=0.24 sample tends to decrease with increasing temperature (∼3 cm$^{-1}$). This result for the x=0.03-0.17 compounds is in good agreement with the structural measurements, which have shown that the Cu-O$_{ap}$ bond is practically independent of temperature or varies by less than 0.2% for all doping levels[15]. For the overdoped x=0.24 compound the disagreement for the overdoped region has also been observed at RT as a function of doping[8], where the Cu-O$_{ap}$ bond decreases with increasing Sr concentration together with the energy of the apex oxygen mode.

Bianconi et al. in an EXAFS study has evaluated the Cu-O$_{xy}$ and Cu-O$_{z}$ bond lengths of the optimally doped La$_{1.85}$Sr$_{0.15}$CuO$_4$ compound. They have shown that there are two Cu-O$_{xy}$ bond lengths that differ by 0.08 to 0.14Å, depending on the temperature of the material. Also, two different Cu-O$_{xy}$ bonds have been observed for this material, but only for temperatures below 100 K (i.e. in the orthorhombic phase), whereas the tilting angle of the octahedra was found to be larger. From their energies, the bands at ∼370 cm$^{-1}$ could be assigned to IR-active phonons. In the tetragonal phase (D$_{4d}$) is symorphic with inversion center the Cu site. Since no symmetry lowering has been observed in the crystallographic studies of these materials, the appearance of new modes denotes a local symmetry breaking of the tetragonal structure. This symmetry breaking can be induced by the partial substitution of Sr for La, but then it should be present in any concentration of Sr continuously increasing with the amount of doping, which does not agree with our Raman data (absence of the ∼370 cm$^{-1}$ mode and substantial reduction in the intensity of the ∼150 cm$^{-1}$ for x=0.24, Fig.2c).

From their energies, the bands at ∼150 cm$^{-1}$ and ∼370 cm$^{-1}$ could be assigned to IR-active phonons. In the E//ab polarization IR spectra of the tetragonal phase a doubly degenerate E$_{u}$ mode exists at ∼140 cm$^{-1}$[12], attributed to the vibrations of the apex oxygen atoms parallel to the ab-plane. In the orthorhombic phase the degeneracy is removed and for x=0.0 the E$_{u}$ mode splits to one at ∼113 cm$^{-1}$ of B$_{2u}$ symmetry (vibrations of the O$_{ap}$ atoms along the b-axis) and another at 140 cm$^{-1}$ of B$_{3u}$ symmetry (vibrations of the O$_{ap}$ atoms along the a-axis)[12]. The XRD measurements have shown[13], that the b-axis increases substantially in the orthorhombic phase. Therefore, the above splitting depends on the amount of orthorhombic distortion reducing to zero in the tetragonal phase. In the Raman spectra of the orthorhombic phase the ∼150 cm$^{-1}$ band appears at low temperatures as a double or triple peak. The new mode at ∼144 cm$^{-1}$ becomes very narrow and the other one at...
\(\sim 125\text{ cm}^{-1}\) very broad at low temperatures and doping levels \(x=0.092-0.17\) (Fig.2b, c, and d). Besides, there are traces of a peak at \(\sim 170\text{ cm}^{-1}\), which could correspond to another IR mode \(\Gamma_7\) (Fig.2a). The apparent increment of the total width of the \(\sim 150\text{ cm}^{-1}\) band with decreasing temperature for the \(x=0.092-0.17\) samples (Fig.8) obviously reflects modifications in the width and intensity of the split modes.

Our data in Fig.2 indicate that the splitting of the \(\sim 150\text{ cm}^{-1}\) band occurs in the range 200-250 K for \(x=0.092, 150-200\text{ K}\) for \(x=0.125\), and \(150-200\text{ K}\) for \(x=0.17\). In the \(x=0.20\) and 0.24 samples, the structural measurements have shown a tetragonal structure at any temperature and the \(\sim 125\text{ cm}^{-1}\) wide mode does not appear to the lowest temperatures (Fig.2e). In the \(x=0.03\) compound the \(\sim 150\text{ cm}^{-1}\) band is hardly observed (Fig.2a), while for \(x=0.07\) the wide mode at \(\sim 125\text{ cm}^{-1}\) is detected above 125 K. Once the mode at \(\sim 144\text{ cm}^{-1}\) (that can be associated with the IR mode of symmetry vibrations of the \(O_2\) atoms along the a-axis) appears it does not vary in energy with decreasing temperature. On the other hand, the mode at \(\sim 125\text{ cm}^{-1}\) (associated with the vibrations of the \(O_2\) atoms along the b-axis) becomes broader and softens at decreasing temperatures. This could be due to the appearance of another IR mode at lower energy \(\Gamma_7\). The Raman spectra with the many new lines that appear at low temperatures are very reminiscent of the formation of stripes in related compounds \(\Gamma_7\) and fits very well with the findings of Bianconi et al. \(\Gamma_7\). The charge ordering is expected to give rise to the formation of a superlattice, lowering the crystal symmetry and bringing edge phonons to the \(\Gamma\) point. Neutron scattering data on \(LaCuO_4\) have found a mode of \(\Delta_{g}\) symmetry at the \(X\) point from the \(La\) atoms of similar energy with the \(150\text{ cm}^{-1}\) band \(\Gamma_7\). Therefore, the observed multiple modes could also be due to such folded phonons unambiguously defining the formation of stripes.

Concerning the possible assignment of the \(\sim 370\text{ cm}^{-1}\) band to a phonon, it can be seen that in the IR spectra of the tetragonal phase a \(q\geq 0\) mode of \(E_u\) symmetry appears at a similar energy \(\sim 360\text{ cm}^{-1}\) [2, 12]. This mode has been attributed to the bond bending oxygen vibrations in the \(CuO_2\) plane and, when the orthorhombic distortion takes place, it splits to one \(B_{3u}\) at \(\sim 353\text{ cm}^{-1}\) and another \(B_{3u}\) mode at \(364\text{ cm}^{-1}\) [12]. Such splitting is not obvious in the Raman spectra, but, as it is mentioned previously, the \(\sim 370\text{ cm}^{-1}\) band is broad \(\sim 30\text{ cm}^{-1}\) (see Fig.9) and, also, seems to have some structure in the low temperature spectra of the orthorhombic phase (Fig.2c). The fitting of this band with two Lorentzians results in two peaks that differ by \(\sim 5-15\text{ cm}^{-1}\), which agrees with the splitting of the two IR-active modes. Thus, the \(\sim 370\text{ cm}^{-1}\) band could be another IR active mode that appears in the \(xx/yy\) Raman spectra because of the symmetry breaking. It should be noted that the largest splitting \(\sim 15\text{ cm}^{-1}\) of the \(\sim 370\text{ cm}^{-1}\) band is observed for the underdoped compound \(x=0.03\) at low temperatures, the main reason being the large value of orthorobicity, which makes the \(b\) axis much larger than the \(a\) axis for this sample \(\Gamma_7\). The energy of the \(B_{3u}\) vibrations of the \(Cu-O_{x/y}\) bond along the \(b\) axis is expected to be lower than the energy of the \(B_{3u}\) vibrations along the \(a\) axis. Also, the average softening of the total band at \(\sim 370\text{ cm}^{-1}\) with decreasing temperature that has been observed for the \(x=0.03\) sample (see Fig.9) could be due to a decrease of the energy of the \(B_{3u}\) mode, since the difference between the \(b\) and \(a\) axes increases with decreasing temperature \(\Gamma_7\). The latter can also explain the increase of the bandwidth for temperatures below \(\sim 50\text{ K}\) compared with other concentrations. If we assume the formation of stripes and the folding of the Brillouin zone, an edge phonon that could be related with the \(\sim 370\text{ cm}^{-1}\) band would be an \(X\) point mode of similar energy related with the apical oxygen \(\Gamma_7\).

The mode at \(\sim 370\text{ cm}^{-1}\) gains intensity together with the broad band at \(\sim 280\text{ cm}^{-1}\), and the wide mode at \(\sim 125\text{ cm}^{-1}\), which appear mainly at low temperatures (Fig.2). In previous IR studies there is a weak \(B_{3u}\) phonon at \(\sim 270\text{ cm}^{-1}\) [2, 12] attributed to the vibrations of the \(Cu\) atoms in the \(ab\) plane [12]. The broad band at \(\sim 280\text{ cm}^{-1}\) has not been observed in the IR spectra of the doped \(La_{2-x}Sr_xCO_3\) compounds [2, 12, 20]. In our compounds this band does not appear in the Raman spectra of the underdoped \(x=0.03\) concentration even at very low temperatures (Fig.2a). It shows-up with increasing \(Sr\) concentration and appears even in the high temperature spectra of the tetragonal phase of the \(x=0.07, 0.092, 0.125\), and 0.17 samples. For the overdoped compounds \(x=0.20\) and 0.24, which are expected to be tetragonal at any temperature, this band is absent to the lowest temperature studied (Fig.2e). Based on its behavior, it is not possible to assign the very broad \(\sim 280\text{ cm}^{-1}\) band to a specific IR mode activated in the Raman spectra from the breaking of symmetry. McQueeney et al. based on inelastic neutron scattering of \(La_{2-x}Sr_xCuO_4\) \((0.8<\leq 0.15)\) at \(10\text{ K}\) (orthorhombic phase) have reported a systematic development of anomalous phonon bands near the doping that induces metal to insulator phase transition [21]. From their phonon density of states (PDOS) data, it can be seen that the metal-insulator transition affects the low energy region, where a band near \(30\text{ meV}\) develops close in energy to the \(280\text{ cm}^{-1}\) band that appears in the Raman spectra. Also, the intensity of \(\sim 30\text{ meV}\) is maximized for optimally doped samples, just like the \(280\text{ cm}^{-1}\) mode. Inelastic neutron scattering measurements showed that the \(\sim 30\text{ MeV}\) band is not caused by electrostatic impurity effects from \(Sr\) substitution [22]. This band has not been observed in any of the Raman measurements performed on samples with \(x=0.0-0.13\) and becomes obvious for higher doping levels. Since the broad band at \(\sim 280\text{ cm}^{-1}\) always appears together with the splitting of the \(\sim 150\text{ cm}^{-1}\) and the wide mode at \(\sim 125\text{ cm}^{-1}\), and its energy fits well with the combination energies of the two modes at \(\sim 125\text{ cm}^{-1}\) and the \(\sim 144\text{ cm}^{-1}\), it is possible to be related with a peak in the PDOS.
Its appearance mainly at low temperatures whenever the multiple modes around 150 cm\(^{-1}\) develop, could also indicate that it might originate from quasiparticle scattering, which in the Raman spectra would create such a high energy peak 18.

Finally we examine the dependence of the relative intensity of the ~150, 370, and 280 cm\(^{-1}\) bands over the intensity of the apex phonon at various temperatures. It is already known that there is an apparent correlation of the intensity of the ~150 cm\(^{-1}\) peak with the variation of the superconducting transition temperature \(T_c\) with Sr content 6. Figure 13 shows the variation of the above mode intensities at various temperatures (concerning the ~280 cm\(^{-1}\) band the room temperature data are not included, since this peak has been observed systematically only in the low temperature spectra). It can be easily seen that the above mentioned correlation with \(T_c\) persists even at the lowest temperature studied (10 K).

\textit{From the above results, it can be seen that these intensities mainly depend on the amount of doping and the local lattice distortions induced by doping.} Another important effect is the temperature where the broad band at ~280 cm\(^{-1}\) and the splitting of the band at ~150 cm\(^{-1}\) appear (Fig.2), which varies with doping; it vanishes for \(x<0.05\) or \(x\geq0.20\) and shows a maximum around optimal doping.

As it is already mentioned above, Bianconi et al. has proposed the existence of charge stripes in the optimally doped LSCO, supporting the ‘two component’ model, where, at optimum doping with 0.2 hole/Cu sites, a first component with hole density \(\delta_1 \sim 0.16\) coexists with another component of impurity states with \(\delta_2 \sim 0.04\), spatially separated in two different types of stripes forming a superlattice of quantum wires 14. It is known that charge stripes break translational (perpendicular to the stripes) and rotational symmetry 28. The appearance of the above mentioned modes in the Raman spectra seems to be induced by a symmetry breaking.

On the other hand, it was suggested that the formation of Jahn-Teller real space pairing can induce a local breaking of symmetry and the appearance of symmetry-forbidden modes in the Raman spectra 25. The formation of such extended polaron complexes is related with stripes and it has a doping dependence that resembles the variations observed, i.e. the splitting of the ~150 cm\(^{-1}\) band and the appearance of the broad peak at ~280 cm\(^{-1}\) in the doping range 0.20\(>x>0.03\). It seems likely that below a certain temperature the preformed polarons create a long range order in one direction only and the modes split into a narrow and a broad band 18,25. One cannot exclude also the possibility that spin stripes are formed, which break the spin-rotational and time reversal invariance 26 and coexist with a charge order 27.

\section*{CONCLUSIONS}

In this work it is shown that the \(\Lambda_x\) mode at ~100 cm\(^{-1}\) shows a classical soft mode behavior even for high Sr-doped compounds (up to \(x=0.17\)), supporting its correlation with the LTO→HTT transition for the Sr contents studied. Also, the mode at ~270 cm\(^{-1}\) of \(\Lambda_x\) symmetry due to vibrations of the plane oxygens along the c axis correlates with the structural phase transition since it appears only in the spectra of the orthorhombic phase. Further, the energy of this mode varies with temperature contrary to the results of previous works.

The low temperature measurements have shown that the behavior of the energy and the asymmetry of the apex phonon should be due to local lattice distortions, which are doping induced. The modification of the relative intensity of the La/Sr and the apex phonons seems to be correlated with the carrier concentration on the CuO\(_2\) planes and consequently with the superconducting transition temperature.

The bands at ~150 and 370 cm\(^{-1}\) that appear in the xx/yy polarization spectra are related with a symmetry breaking that occurs at temperatures that scale with \(T_c\). The first band splits in at least two modes from which, one is very narrow and the other very wide and the spectra are reminiscent of those obtained from the formation of stripes. Another broad band was observed in the xx/yy polarization spectra at ~280 cm\(^{-1}\), which appears to scale with the \(T_c\) dependence on doping. This is probably due to a peak in the phonon density of states or to quasiparticle scattering. Moreover, the correlation of the relative intensity of the bands at ~150 and 370 cm\(^{-1}\) with the Sr concentration for maximum \(T_c\) that was found at room temperature seems to persist at the lowest temperature studied. A similar connection exists between the intensity of the ~280 cm\(^{-1}\) band and the doping. All these results can be attributed to the formation of stripes at temperatures well above the transition temperature and for doping levels where the compound is superconducting.

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Figure 1. Typical Raman spectra for selected temperatures for the x=0.03 (a), x=0.092 (b), x=0.125 (c), x=0.17 (d), and x=0.24 (e) samples in the y(zz)̅ scattering geometry using the 514.5 nm excitation wavelength.

Figure 2. Typical Raman spectra for selected temperatures for the x=0.03 (a), x=0.092 (b), x=0.125 (c), x=0.17 (d), and x=0.24 (e) samples in the y(zz)̅ scattering geometry using the 514.5 nm excitation wavelength.

Figure 3. Dependence of the energy (a) and the linewidth (b) on temperature for the soft phonon observed in y(zz)̅ scattering geometry spectra for x=0.03, 0.092, 0.125, 0.17, and 0.24.

Figure 4. The dependence of the soft phonon (a) energy and (b) linewidth on doping at various temperatures.

Figure 5. The dependence on temperature of the (a) La/Sr and (b) apex phonon energy for the x=0.03, 0.092, 0.125, 0.17, and 0.24 samples.

Figure 6. The dependence on temperature of the (a) La/Sr and (b) apex phonon linewidth for the x=0.03, 0.092, 0.125, 0.17, and 0.24 samples.

Figure 7. The relative intensity of the La/Sr phonon to the apex one as a function of temperature for the x=0.03, 0.092, 0.125, 0.17, and 0.24 samples.

Figure 8. (a) Energy and (b) linewidth dependence on temperature for the mode at ~150 cm⁻¹ observed in y(xx)̅̅̅̅ scattering geometry spectra for x=0.092, 0.125, 0.17, 0.20, and 0.24.

Figure 9. (a) Energy and (b) linewidth dependence on temperature for the mode at ~370 cm⁻¹ observed in y(xx)̅̅̅̅ scattering geometry spectra for x=0.03, 0.092, 0.125, 0.17, 0.20, and 0.24.

Figure 10. (a) Energy and (b) linewidth dependence on temperature for the mode at ~280 cm⁻¹ observed...
in $y(xx)\bar{y}$ scattering geometry spectra for $x=0.03, 0.092, 0.125, 0.17$, and $0.24$.

Figure 11. The dependence of the apex phonon asymmetry on doping, at various temperatures.

Figure 12. The dependence of the relative intensity $\text{La}/\text{apex}$, on doping at various temperatures.

Figure 13. The dependence of the relative intensities (a) $150\text{ cm}^{-1}/\text{apex}$, (b) $370\text{ cm}^{-1}/\text{apex}$, and (c) $280\text{ cm}^{-1}/\text{apex}$ on doping at various temperatures.
La$_{1.97}$Sr$_{0.03}$CuO$_4$  
(zz) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)
La$_{1.908}$Sr$_{0.092}$CuO$_4$

(zz) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)

100 200 300 400 500

1b
\( \text{La}_{1.875}\text{Sr}_{0.125}\text{CuO}_4 \) (zz) Polarization

\begin{align*}
295K \\
250K \\
200K \\
150K \\
100K \\
90K \\
50K \\
10K \\
\end{align*}
La$_{1.83}$Sr$_{0.17}$CuO$_4$

(zz) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)

1d
La$_{1.76}$Sr$_{0.24}$CuO$_4$ (zz) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)

100 200 300 400 500

295K
250K
200K
150K
120K
90K
70K
50K
30K
10K
La$_{1.97}$Sr$_{0.03}$CuO$_4$

(xx) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)

295K
200K
150K
120K
90K
50K
10K
La\textsubscript{1.908}Sr\textsubscript{0.092}CuO\textsubscript{4}

(xx) Polarization

295K

250K

200K

150K

90K

50K

10K

Intensity (arb. units)

Raman Shift (cm\textsuperscript{-1})

\textbf{2b}
La$_{1.875}$Sr$_{0.125}$CuO$_4$

(xx) Polarization
La$_{1.83}$Sr$_{0.17}$CuO$_4$

(xx) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)
La$_{1.76}$Sr$_{0.24}$CuO$_4$

(xx) Polarization

Intensity (arb. units)

Raman Shift (cm$^{-1}$)

295K

250K

150K

70K

50K

10K

La$_{1.76}$Sr$_{0.24}$CuO$_4$
La$_{2-x}$Sr$_x$CuO$_4$

Soft Mode

Fig. 3
Fig. 4

Soft mode energy (cm$^{-1}$) vs Sr Content (x)

- $T=200$ K
- $T=150$ K
- $T=50$ K
- $T=10$ K
Fig. 5

(a) La/Sr mode energy (cm\(^{-1}\))

(b) Apex mode energy (cm\(^{-1}\))

Temperature (K)
Fig. 6
Fig. 7

zz Polarization

Relative Intensity La/apex vs Temperature (K)
Fig. 8
Mode at ~370 cm$^{-1}$

Fig. 9
Fig. 10

(a) Broad mode at ~280 cm$^{-1}$

(b)
Fig. 11: Apex phonon asymmetry (zz-polarization) vs. Sr Content (x) at various temperatures:
- T=300 K
- T=200 K
- T=150 K
- T=50 K
- T=10 K
Fig. 12
Fig. 13b
Fig. 13c