Micro-Raman evidence for topological charge order across the superconducting dome of $La_{2-x}Sr_xCuO_4$

D. Lampakis and E. Liarokapis
Department of Physics, National Technical University, GR-15780 Athens, Greece

C. Panagopoulos
Cavendish Laboratory and IRC in Superconductivity, University of Cambridge, Madingley Road, CB3 0HE, United Kingdom
(Received 28 January 2006; published 19 May 2006)

The doping dependence of the micro-Raman spectra of high-quality $La_{2-x}Sr_xCuO_4$ microcrystals with $x=0.0$–0.45 has been investigated in the region 10–300 K. The phonon at ~ 100 cm^{-1} of the orthorhombic phase shows a classical soft-mode behavior up to $x=0.17$, supporting its correlation with the low-temperature orthorhombic to high-temperature tetragonal transition. In the *xx-yy* polarization spectra of the superconducting concentrations new modes at ~ 150 and 370 cm^{-1} related to the symmetry breaking and a broad band at ~ 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 ~ 150, ~ 280, and ~ 370 cm^{-1}, the intensity of the La/Sr mode, and the asymmetry of the apex phonon.

DOI: 10.1103/PhysRevB.73.174518 PACS number(s): 74.72.−h, 78.30.−j, 63.20.−e

INTRODUCTION

It is known that the $La_{2-x}Sr_xCuO_4$ (LSCO) superconductor shows a variety of phases with doping and temperature.[1] One of the main conclusions from Raman investigations of the vibrational modes of La_2CuO_4 has been the existence of a soft mode at ~ 100 cm^{-1} (12 meV) of A_g symmetry, attributed to tilting vibrations of the CuO_6 octahedra about the diagonal (110) axis.[2–4] This mode has been correlated with the observed high-temperature tetragonal (HTT) to low-temperature orthorhombic (LTO) structural phase transition of LSCO (Ref. 5) and has been studied for Sr-doped samples, up to $x=0.07$.[2,3,6] As the structural critical temperature decreases with increasing Sr content,[1] the soft mode can only be observed at LT and it has not been studied for $x>0.07$. Here we examine the behavior of the soft mode for even higher Sr concentrations and, particularly, for x values near optimum.

The two strong modes of this compound are of A_g symmetry and have been attributed to the vibrations of the La/Sr and the apex oxygen (O_z) atoms along the c axis. Their dependence on temperature has been studied for a wide range of Sr doping. Our studies of these materials at room temperature (RT) have shown that the asymmetry of the apex phonon and the relative intensity of the La/Sr phonon over the apex mode show a maximum for the Sr concentrations at which the compound appears with the maximum transition temperature to superconductivity.[6] It was concluded that, since this effect cannot be assigned to any apparent structural changes of the system, it might originate from a charge redistribution, which occurs at temperatures well above T_c and affects the electronic states and the polarizabilities of the La/Sr and apex atoms at some critical Sr concentration. For this reason, it was interesting to examine how this correlation of some phonon characteristics with the transition temperature evolves at low temperatures.

Furthermore, we found that, with increasing x two symmetry-forbidden broad modes at ~ 150 and ~ 370 cm^{-1} appear in the *xx-yy* polarization Raman spectra, despite the phase transition from the orthorhombic to the more symmetric tetragonal phase.[2,3] In the low-temperature spectra a broadband at ~ 280 cm^{-1} has been also observed.[2] A common feature of these peaks is that their intensity shows a maximum for the optimally doped samples.[6] In this work we have investigated the temperature dependence of the Raman spectra for various Sr contents and compare with previously reported room-temperature data.

EXPERIMENTAL SETUP

Individual microcrystallites from a selected series of high-quality $La_{2-x}Sr_xCuO_4$ 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 axes could not be discriminated in the twinned samples) at nominal temperatures from 10 K to RT with a Jobin-Yvon T64000 triple spectrometer, equipped with a liquid-nitrogen-cooled charge-coupled-device (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 wavelength of an Ar^+ laser was used for excitation at a power level of ≤ 0.1 mW/μm^2. 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 h, 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 $y(zz)\bar{y}$ and $y(xx)\bar{y}$ [or $x(yy)\bar{x}$] polarization, are shown in

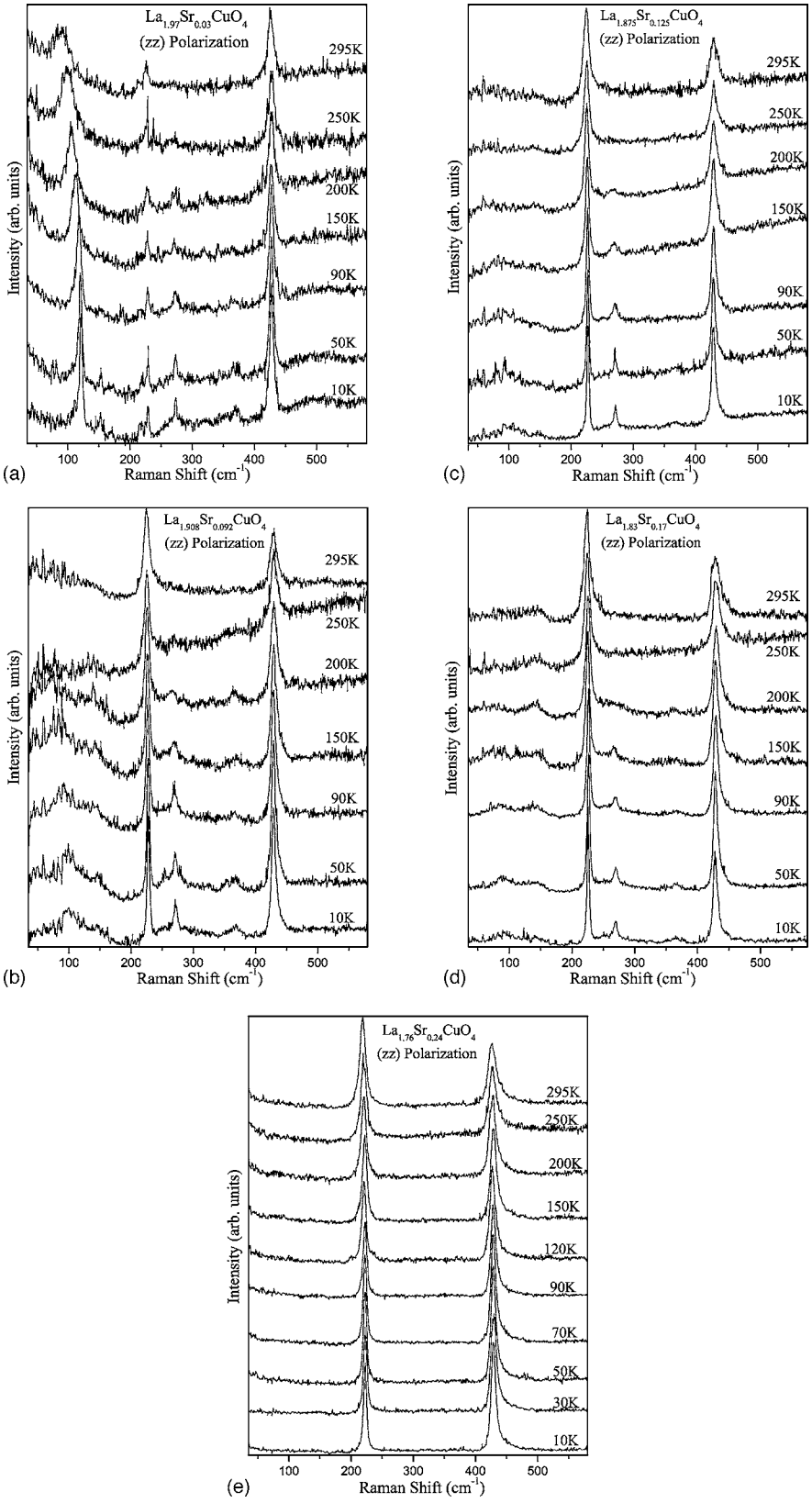

FIG. 1. Typical Raman spectra for selected temperatures for the $x=0.03$ (a), $x=0.092$ (b), $x=0.125$ (c), $x=0.17$ (d), and $x=0.24$ (e) samples in the $y(zz)\bar{y}$ scattering geometry using the 514.5-nm excitation wavelength.

Figs. 1 and 2, respectively. In all cases, the two strong La/Sr and apex oxygen phonons of A_g symmetry appear. According to the $La_{2-x}Sr_xCuO_4$ phase diagram, the structural critical transition temperature T_{ot}, for the insulating $La_{1.97}Sr_{0.03}CuO_4$ sample is $\sim$560 K.[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. 1(a)]. The mode at $\sim$270 cm^{-1} attributed to the vibrations of the plane oxygens along the c axis is observed in all zz spectra of Fig. 1(a). This

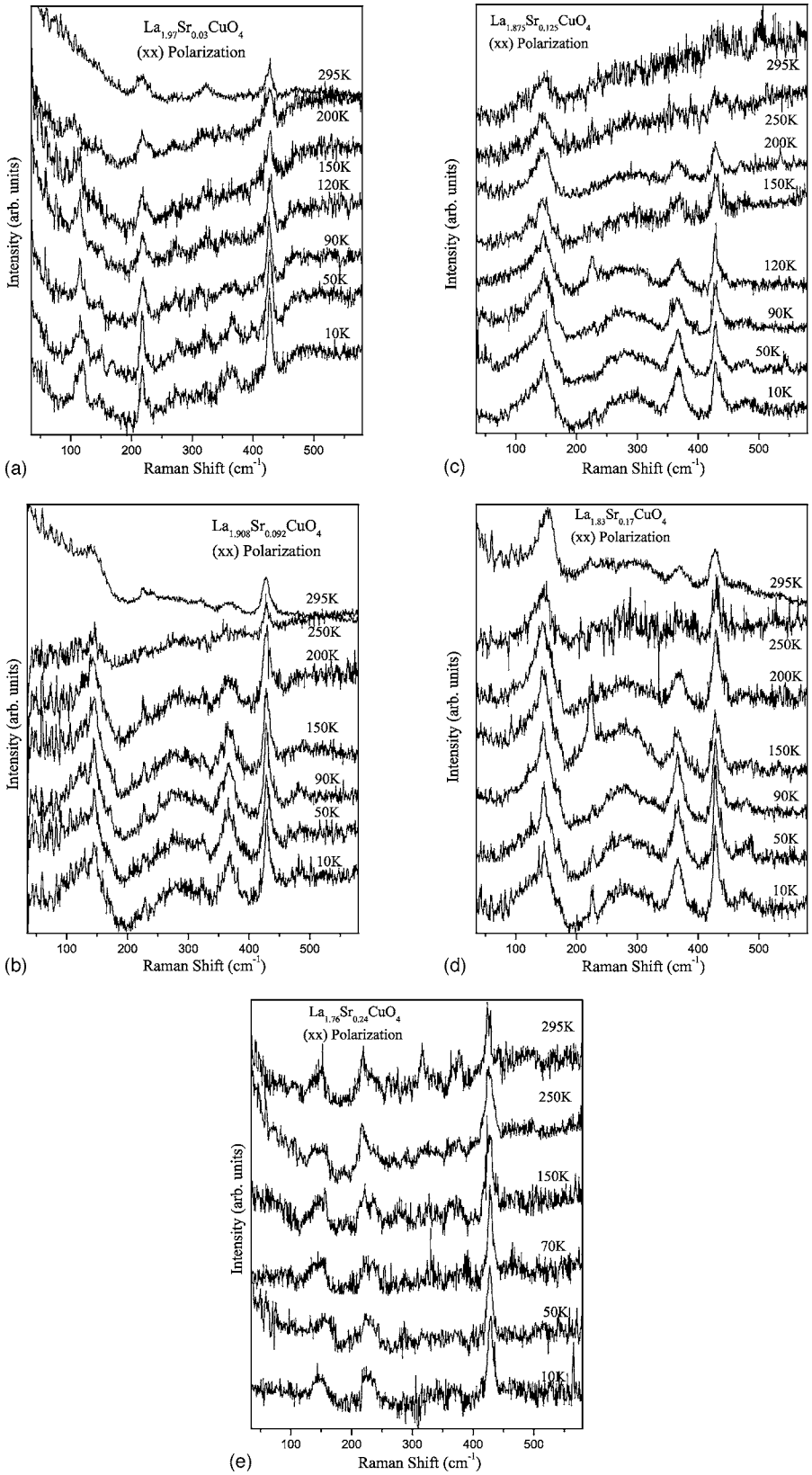

FIG. 2. Typical Raman spectra for selected temperatures for the $x=0.03$ (a), $x=0.092$ (b), $x=0.125$ (c), $x=0.17$ (d), and $x=0.24$ (e) samples in the $y(xx)\bar{y}$ [or $x(yy)\bar{x}$] scattering geometry using the 514.5-nm excitation wavelength.

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.[2,3,7] Concerning the *xx-yy* polarization spectra for the $x=0.03$ sample [Fig. 2(a)], 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. 1(a)]. With increasing doping these two bands appear at much higher temperatures, even at RT in the spectra of the superconducting materials [tetragonal phase, Figs.

2(b)–2(e)]. Therefore, their appearance cannot be related with the HTT→LTO structural phase transition. Besides, a weak mode at ~320 cm^{-1} of A_{1g} symmetry[3] is present in the *xx-yy* spectra with energy independent of temperature [Fig. 2(a)]. A broad continuum around 280 cm^{-1} is also present at low temperatures and for intermediate doping in the same polarization spectra [Figs. 2(c) and 2(d)]. Finally, the mode at ~100 cm^{-1} rapidly softening with increasing temperature [Fig. 2(a)] is apparently an escape from the *zz* polarization.

In the *zz* polarization spectra of the underdoped superconductor $La_{1.908}Sr_{0.092}CuO_4$ with T_{ot}~300 K, the modes at ~100 and 270 cm^{-1} are observed only below 250 K [Fig. 1(b)]. 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. 2(b)]. 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 oxygen atoms 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 [Figs. 2(c) and 2(d)]. In $La_{1.76}Sr_{0.24}CuO_4$ the intensity of the three broadbands appears substantially reduced [Fig. 2(e)]. 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. 1(c)]. Concerning the $x=0.17$ sample the soft mode starts appearing in the *zz* spectra at even lower temperatures [Fig. 1(d)], 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 $La_{1.76}Sr_{0.24}CuO_4$ [Fig. 1(e)] 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 $x=0.07$.[2,3,6] In Fig. 3(a) 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. 3(a), the solid lines are best fit to the data with curves $\omega_{soft} \propto (T_{ot}-T)^{1/2}$, which assume a second-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 3(b) 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.

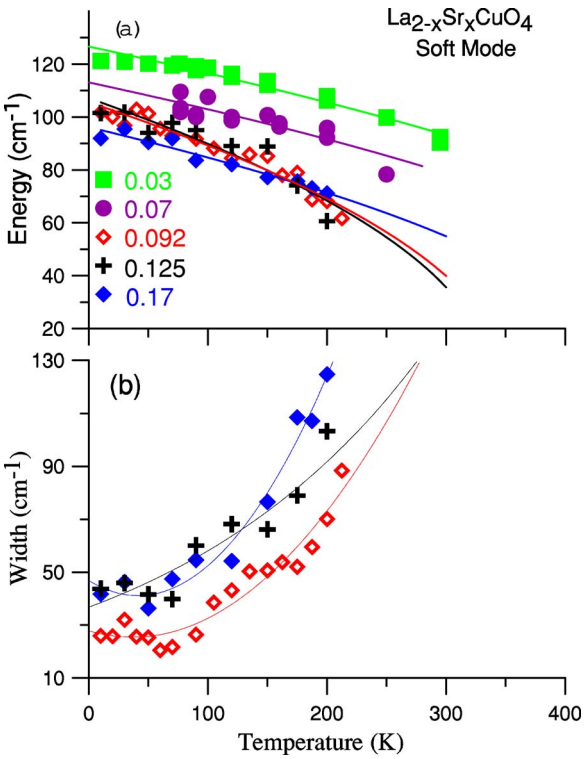

FIG. 3. (Color online) Dependence of the energy (a) and the linewidth (b) on temperature for the soft phonon observed in $y(zz)\bar{y}$ scattering geometry spectra for the $x=0.03$, 0.092, 0.125, and 0.17 samples.

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 [Figs. 1(b)–1(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 oxygen atoms 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. 1(a) 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 ~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

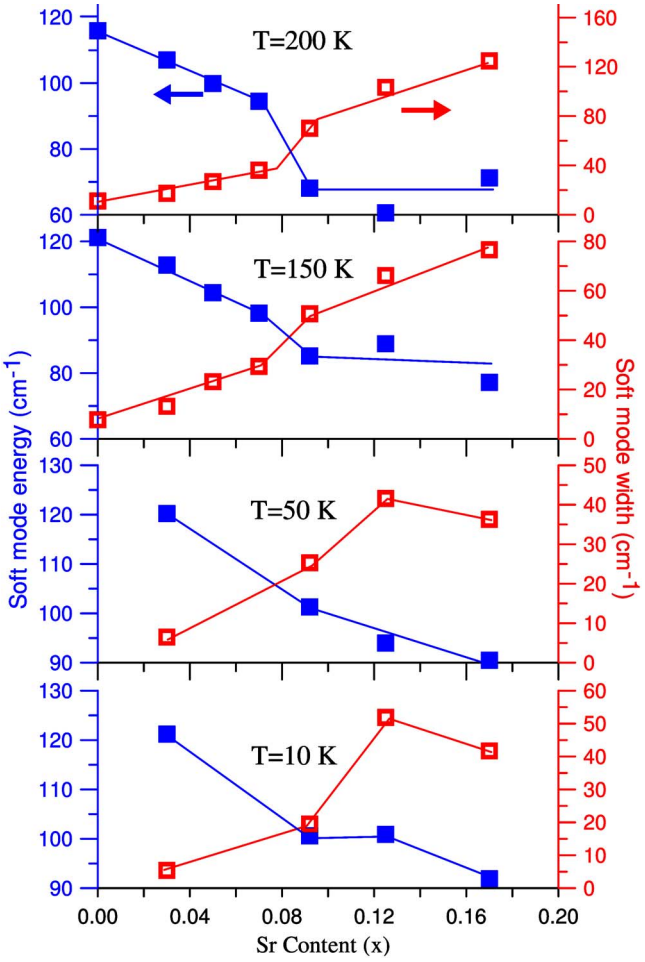

FIG. 4. (Color online) The dependence of the soft phonon energy and linewidth on doping at various temperatures.

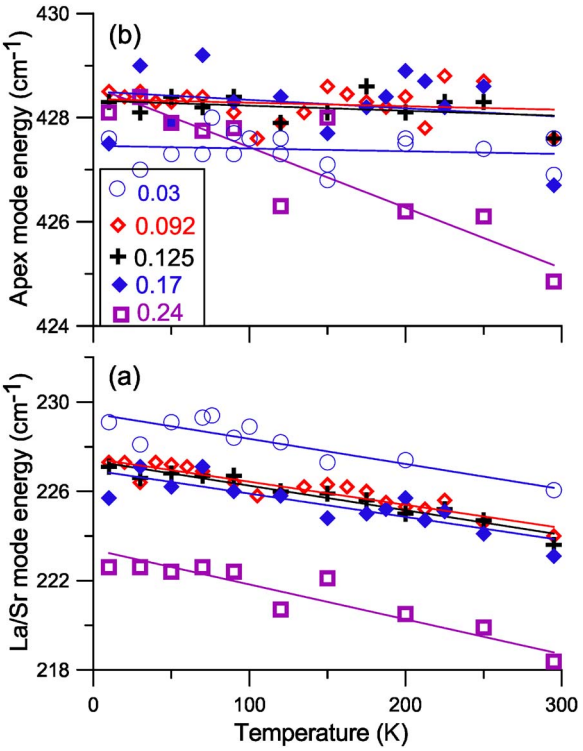

FIG. 5. (Color online) The dependence on temperature of the (a) La/Sr and (b) apex phonon energy for the $x=0.03$, 0.092, 0.125, 0.17, and 0.24 samples.

can be clearly seen that there is an almost linear increase in energy with decreasing temperature of the order ~5–6 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→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 ~100 cm^{-1}.

In Fig. 5(a) 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 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. 5(a)] and underdoped superconducting ($x=0.05,0.07$) compounds.[6] On the contrary, the apex energy remains practically constant with temperature for all compounds in the $x=0.0$–0.17 range [Fig. 5(b) and Ref. 6]. Instead, there is a decrease of approximately 3 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→LTO phase in the temperature range studied. This transition is correlated to 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 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 ~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 to the plateau in the doping dependence of T_c and the charge ordering*.[8] 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 wideband at ~150 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

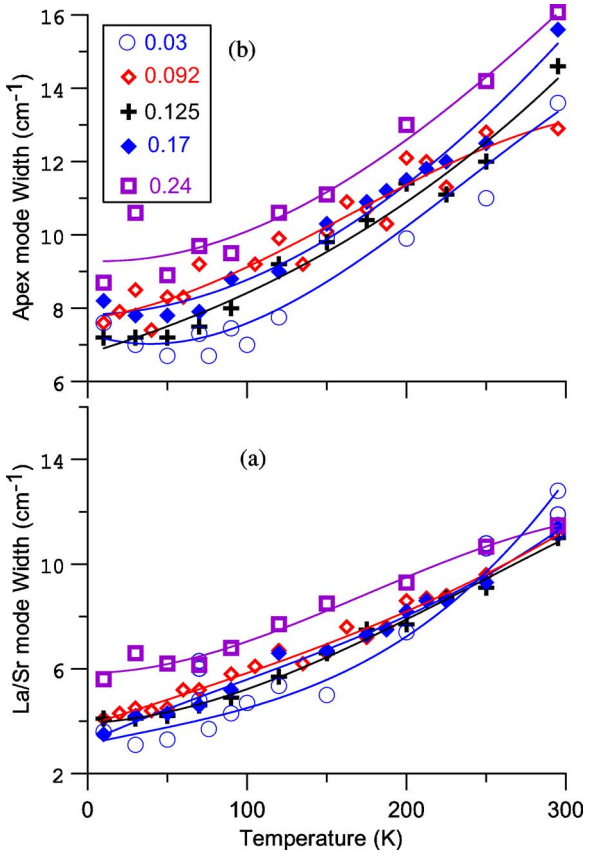

FIG. 6. (Color online) The dependence on temperature of the (a) La/Sr and (b) apex phonon linewidth for the $x=0.03$, 0.092, 0.125, 0.17, and 0.24 samples.

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 Fig. 2 that this band

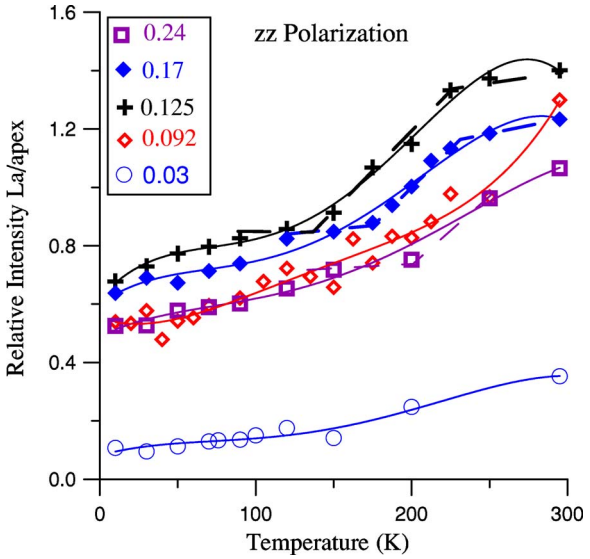

FIG. 7. (Color online) The relative intensity of the La/Sr phonon to the apex one as a function of temperature for the $x=0.03$, 0.092, 0.125, 0.17, and 0.24 samples.

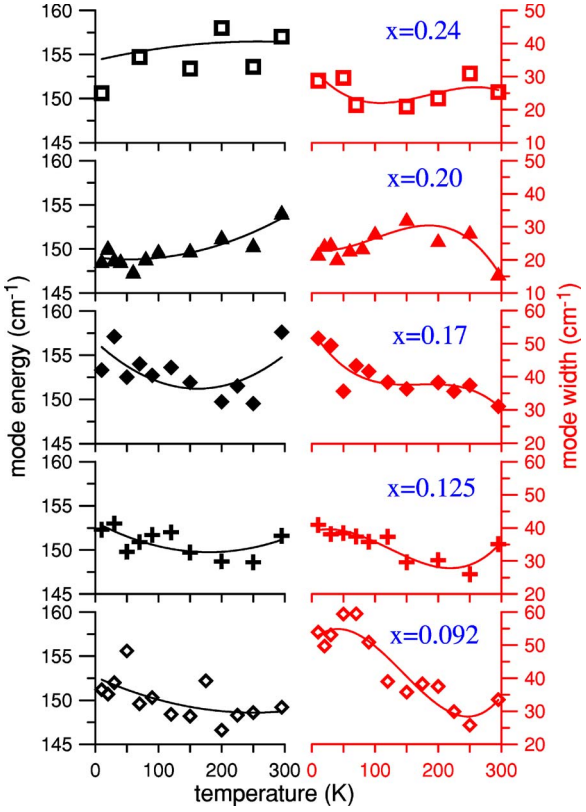

FIG. 8. (Color online) Energy and linewidth dependence on temperature for the mode at ~150 cm^{-1} observed in $y(xx)\bar{y}$ scattering geometry spectra for $x=0.092$, 0.125, 0.17, 0.20, and 0.24.

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 ~370 cm^{-1}. For the $x=0.092$–0.24 compounds the energy and width of the mode seem 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. 2(a)]. The energy of this mode depends strongly on temperature decreasing by ~8 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. 9(b)].

The broadband at ~280 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. 2(d)]. For $x=0.092$ and 0.125 the band is observed for temperatures below 250 K [Figs. 2(b) and 2(c)], while for the $x=0.03$ sample it seems not to be present to the lowest temperatures studied [Fig. 2(a)]. Similar to the ~150 and 370-cm^{-1} broad peaks, the appearance of this band cannot be correlated with Raman active modes or the HTT→LTO phase transition. For $x=0.125$ the transition temperature T_{ot} is nearly the same with the temperature at which the ~280 cm^{-1} band appears, but this is not the case for the $x=0.092$ and $x=0.17$ samples. Besides, the spectra of the x

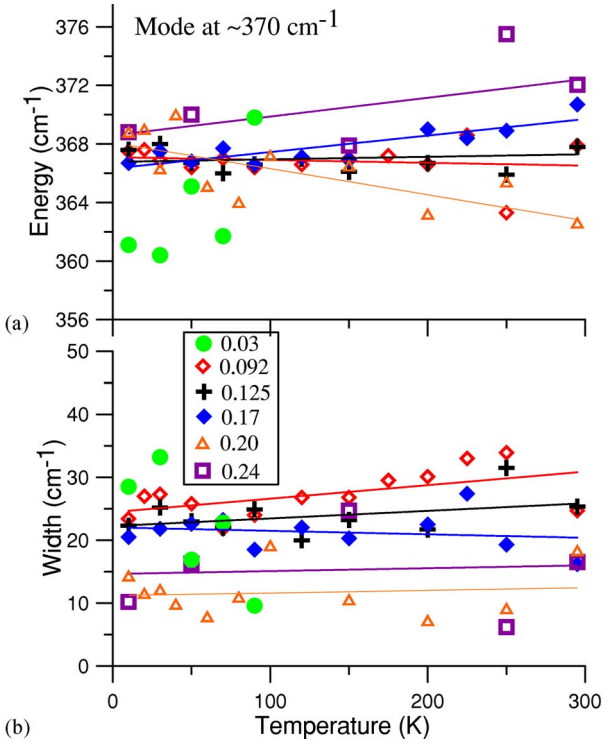

FIG. 9. (Color online) (a) Energy and (b) linewidth dependence on temperature for the mode at ~370 cm^{-1} observed in $y(xx)\bar{y}$ scattering geometry spectra for x=0.03, 0.092, 0.125, 0.17, 0.20, and 0.24.

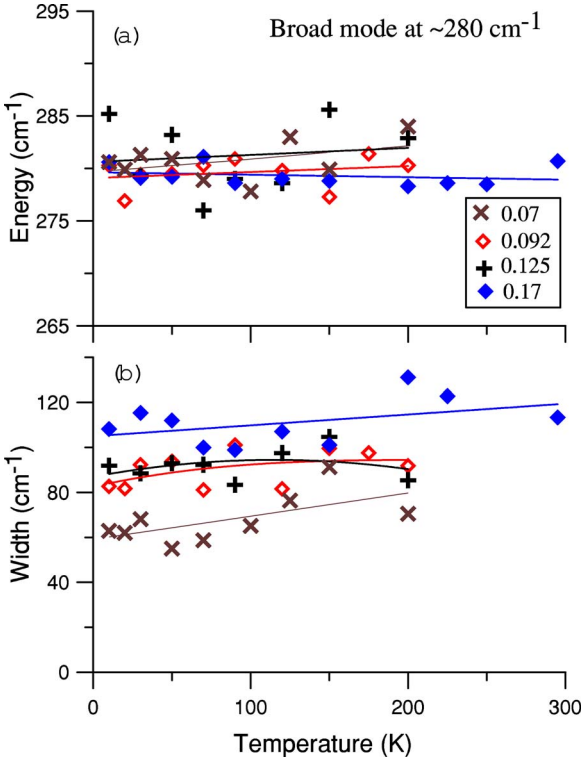

FIG. 10. (Color online) (a) Energy and (b) linewidth dependence on temperature for the mode at ~280 cm^{-1} observed in $y(xx)\bar{y}$ scattering geometry spectra for the x=0.03, 0.092, 0.125, and 0.17 samples.

=0.03 sample, which is orthorhombic even at room temperature, do not show this broadband. For the x=0.092–0.17 compounds, the energy of this band does not vary with temperature within experimental error [Fig. 10(a)], while its width appears to be very large (~100 cm^{-1}) and almost independent of temperature for all samples [Fig. 10(b)].

DISCUSSION

The apex phonon energy shown in Fig. 5 (and from Ref. 6) 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 seems 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_z bond is practically independent of temperature or varies by less than 0.2% for all doping levels.[9] For the overdoped x=0.24 compound the disagreement for the overdoped region has also been observed at RT as a function of doping,[6] where the Cu-O_z bond decreases with increasing Sr concentration together with the energy of the apex oxygen mode.

Bianconi *et al.*[8] in an extended x-ray-absorption fine-structure (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_z bond lengths that differ by 0.08–0.14 Å, 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 the above it was concluded that in the $La_{1.85}Sr_{0.15}CuO_4$ structure apart of the normal (undistorted) there are also distorted octahedra. These local lattice distortions have been attributed to the existence of two types of stripes, the *U*-type, which is due to the undistorted octahedra, and the *D*-type which is due to the distorted ones.[8]

The existence of a shorter Cu-O_z bond would imply another weak phonon peak in the Raman spectra at the high-energy side of the band due to the vibrations of the apex oxygen atoms along the c axis (A_g symmetry). A weak peak could be related with the nonvariation of the apex phonon energy with temperature for the compounds with $x \leq 0.17$. The decrease of the energy of this mode with temperature for the x=0.24 sample would imply the absence of the shorter Cu-O_z bond in the overdoped region. Also, the asymmetry of the A_g apex phonon may originate from doping induced local lattice distortions and the second phonon peak. A correlation has already been established at room temperature between the doping dependence of the asymmetry of this phonon (as observed in the zz polarization) and the relative dependence of T_c.[6] As can be seen in Fig. 11 a similar correlation between the apex phonon asymmetry and T_c exists at the lowest temperatures studied. For the xx-polarization spectra (Fig. 2) the asymmetry of the apex mode is even more pronounced. For x=0.03 and 0.24 there is no asymmetry for all temperatures [Figs. 2(a) and 2(e)], while for the other concentrations the asymmetry of the apex phonon is quite clear.

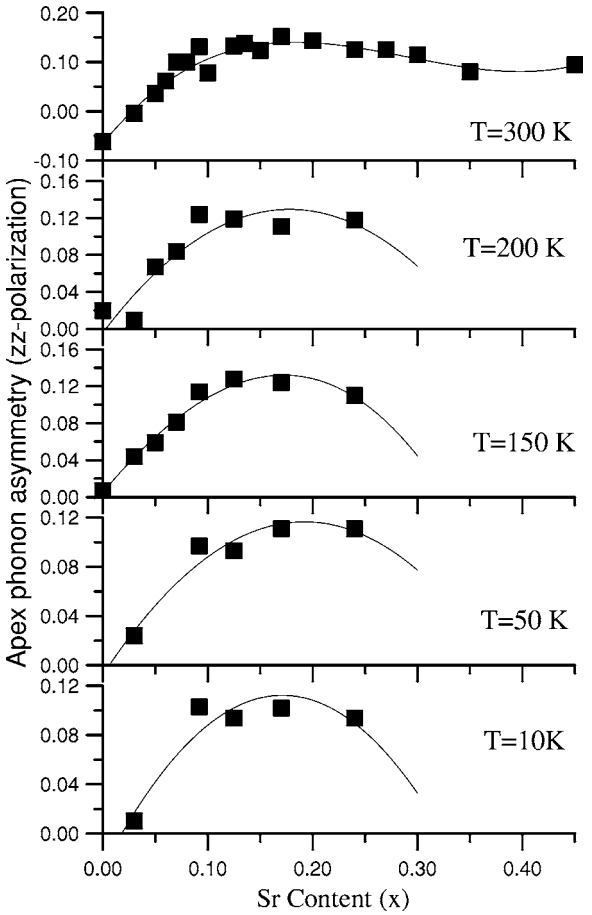

FIG. 11. The dependence of the apex phonon asymmetry on doping, at various temperatures.

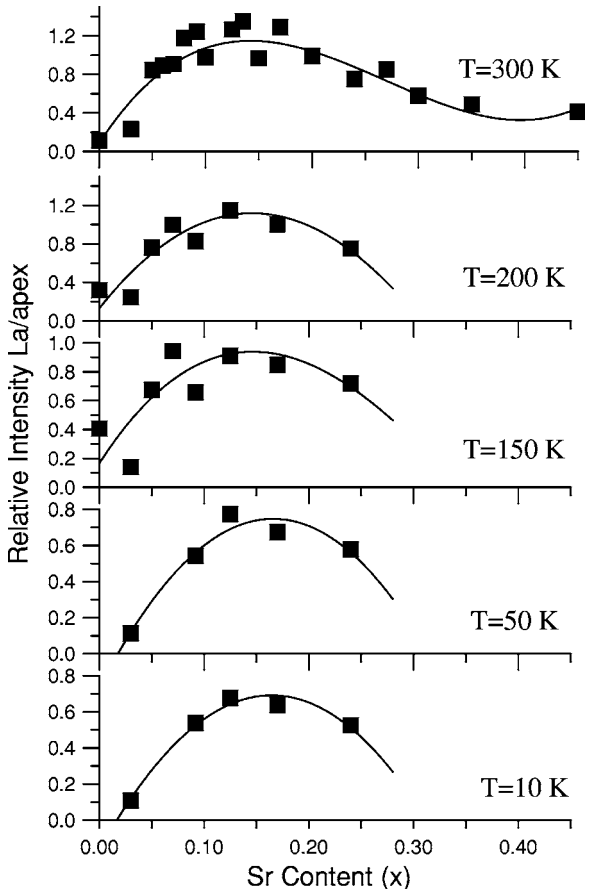

FIG. 12. The dependence of the relative intensity La/apex, on doping at various temperatures.

For $x=0.125$ the apex phonon seems to consist at least of another peak at the high-energy side. This critical concentration corresponds to the plateau in the T_c.

It is known that, at room temperature, the relative intensity of the two strong A_g phonons varies with doping in a similar way as T_c.[6] According to the low-temperature data, the relative intensity La/apex as a function of Sr content reaches a maximum value in the optimally doped region for all temperatures studied (Fig. 12). The substitution of Sr^{2+} for La^{3+} in LSCO adds holes to the compound from the La/Sr sites, with the superconductivity appearing when the carrier concentration at the CuO_2 planes exceeds a limit. The small intensity of the La/Sr A_g phonon for $x \leq 0.03$ in Fig. 12 can be attributed to the local screening of the light due to the high concentration of carriers at these sites. By increasing the amount of doping, the holes at the La/Sr sites are expected to move to the CuO_2 planes reducing the screening effect and, consequently, increasing the La/Sr phonon intensity. With the further increase of doping above optimal the La/apex relative intensity seems to decrease again, but at much less rate than the initial increase for $x=0.0$–0.03 (Fig. 12). It is possible that after the optimal doping the additional carriers can no longer move preferentially to the CuO_2 planes screening equally all phonons.

In the *xx-yy* scattering polarization and for doping concentrations that the compound is in the tetragonal phase and superconducting, new symmetry-forbidden modes appear in the Raman spectra (Fig. 2). The space group of the tetragonal structure (D_{4h}^{17}) 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 $\sim$370-cm^{-1} mode and substantial reduction in the intensity of the $\sim$150 cm^{-1} for $x=0.24$, Fig. 2(e)].

From their energies, the bands at $\sim$150 cm^{-1} and $\sim$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 $\sim$140 cm^{-1},[2,7] 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 $\sim$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).[7] The x-ray diffraction (XRD) measurements have shown,[9] 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 spec-

tra 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 ~125 cm^{-1} very broad at low temperatures and doping levels $x=0.092$–0.17 [Figs. 2(b)–2(d)]. Besides, there are traces of a peak at ~170 cm^{-1}, which could correspond to another IR mode[10] [Fig. 2(a)]. The apparent increment of the total width of the ~150-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 ~150-cm^{-1} band occurs in the range 200–250 K for $x=0.092$, 150–200 K for $x=0.125$, and 150–200 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 ~125-cm^{-1} wide mode does not appear to the lowest temperatures [Fig. 2(e)]. In the $x=0.03$ compound the ~150-cm^{-1} band is hardly observed [Fig. 2(a)], while for $x=0.07$ the wide mode at ~125 cm^{-1} is detected above 125 K. Once the mode at ~144 cm^{-1} (which can be associated with the IR mode of symmetry vibrations of the O_z atoms along the a axis) appears, it does not vary in energy with decreasing temperature. On the other hand, the mode at ~125 cm^{-1} (associated with the vibrations of the O_z 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.[10] The Raman spectra with the many new lines that appear at low temperatures are very reminiscent of the formation of stripes in related compounds[11] and fits very well with the findings of Bianconi *et al.*[8] The charge ordering is expected to give rise to the formation of a superlatice, lowering the crystal symmetry and bringing edge phonons to the Γ point. Neutron scattering data on $LaCuO_4$ have found a mode of A_g symmetry at the X point from the La atoms of similar energy with the 150 -cm^{-1} band.[12] 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 ~370-cm^{-1} band to a phonon, it can be seen that in the IR spectra of the tetragonal phase a $q\simeq 0$ mode of E_u symmetry appears at a similar energy (~360 cm^{-1}).[2,7] 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_{2u} at ~353 cm^{-1} and another B_{3u} mode at 364 cm^{-1}.[7] Such splitting is not obvious in the Raman spectra, but as it is mentioned previously, the ~370-cm^{-1} band is broad (~30 cm^{-1}) (see Fig. 9) and, also, seems to have some structure in the low-temperature spectra of the orthorhombic phase [Fig. 2(c)]. The fitting of this band with two Lorentzians results in two peaks that differ by ~5–15 cm^{-1}, which agrees with the splitting of the two IR-active modes. Thus, the ~370 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 (~15 cm^{-1}) of the ~370-cm^{-1} band is observed for the underdoped compound ($x=0.03$) at low temperatures, the main reason being the large value of orthorhombicity, which makes the b axis much larger than the a axis for this sample.[6,9] The energy of the B_{2u} vibrations of the Cu-O_{xy} 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 ~370 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_{2u} mode, since the difference between the b and a axes increases with decreasing temperature.[9] The latter can also explain the increase of the bandwidth for temperatures below ~50 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 ~370-cm^{-1} band would be an X point mode of similar energy related with the apical oxygen.[12]

The mode at ~370 cm^{-1} gains intensity together with the broadband at ~280 cm^{-1} and the wide mode at ~125 cm^{-1}, which appear mainly at low temperatures (Fig. 2). In previous IR studies there is a weak B_{3u} phonon at ~270 cm^{-1} (Refs. 2 and 7) attributed to the vibrations of the Cu atoms in the ab plane.[7] The broadband at ~280 cm^{-1} has not been observed in the IR spectra of the doped $La_{2-x}Sr_xCuO_4$ compounds.[2,7,13] 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. 2(a)]. 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. 2(e)]. Based on its behavior, it is not possible to assign the very broad ~280-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 $La_{2-x}Sr_xCuO_4$ ($0.0\leq 0.15$) at 10 K (orthorhombic phase) have reported a systematic development of anomalous phonon bands near the doping that induces metal to insulator phase transition.[14] 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 meV develops close in energy to the 280-cm^{-1} band that appears in the Raman spectra. Also, the intensity of ~30 meV is maximized for optimally doped samples, just like the 280-cm^{-1} mode. Inelastic neutron scattering measurements showed that the ~30-MeV band is not caused by electrostatic impurity effects from Sr substitution.[15] This band has not been observed in any of the Raman measurements performed on samples with $x=0$–0.03 and becomes obvious for higher doping levels. Since the broadband at ~280 cm^{-1} always appears together with the splitting of the ~150 cm^{-1} and the wide mode at ~125 cm^{-1}, and its energy fits well with the combination energies of the two modes at ~125 cm^{-1} and the ~144 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.[11]

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

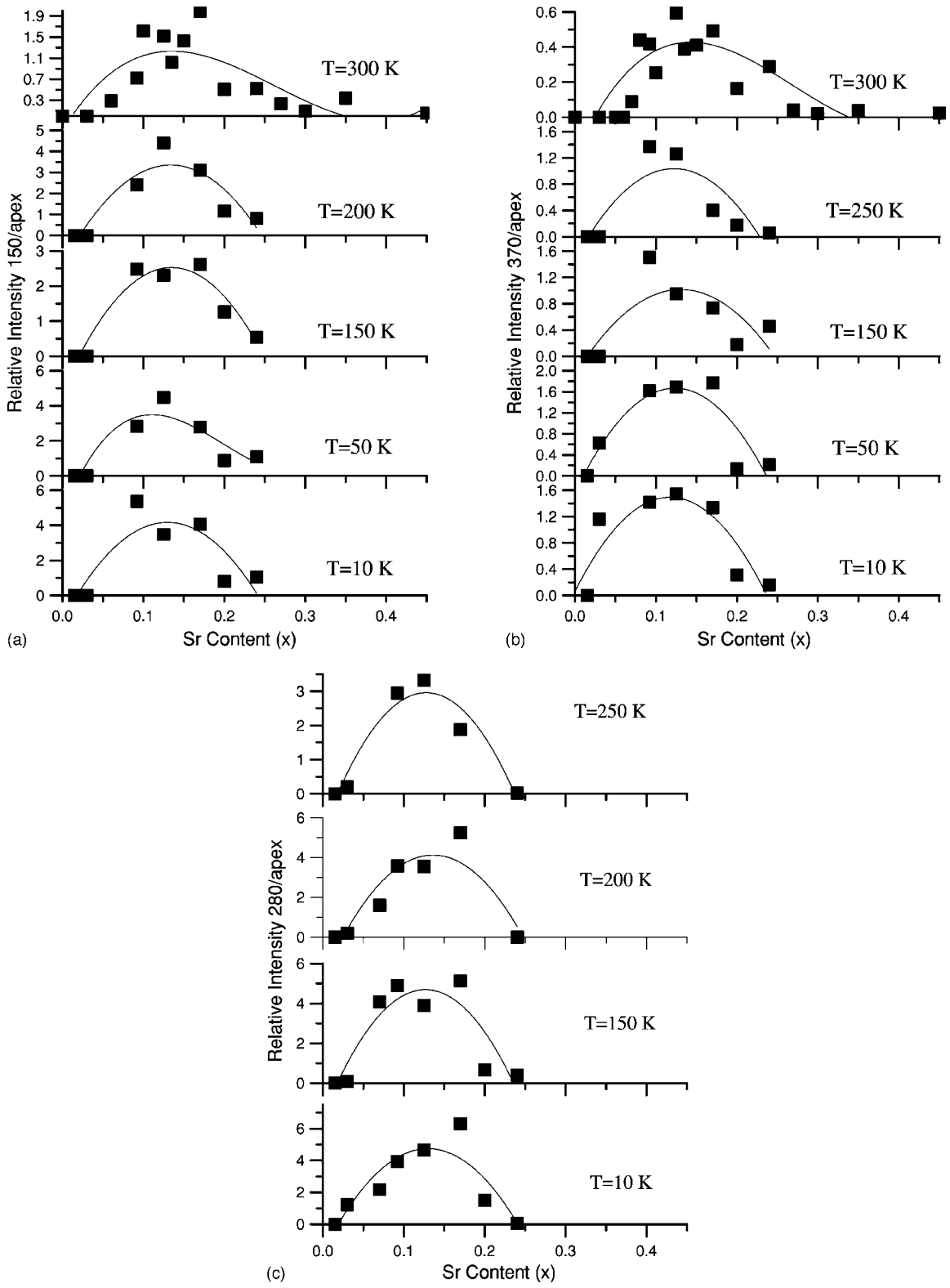

FIG. 13. The dependence of the relative intensities: (a) 150 cm^{-1}/apex, (b) 370 cm^{-1}/apex, and (c) 280 cm^{-1}/apex on doping at various temperatures.

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 correla-

tion with T_c persists even at the lowest temperature studied (10 K). *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 broadband at $\sim 280\ \mathrm{cm}^{-1}$ and the splitting of the band at $\sim 150\ \mathrm{cm}^{-1}$ appear (Fig. 2), which varies with doping; it vanishes for $x < 0.05$ or $x \geq 0.20$ and shows a maximum around optimal doping.

As is already mentioned above, Bianconi *et al.* have 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 $\delta_i \sim 0.16$ coexists with another component of impurity states with $\delta_l \sim 0.04$, spatially separated in two different types of stripes forming a superlattice of quantum wires.[8] It is known that charge stripes break translational (perpendicular to the stripes) and rotational symmetry.[16] 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.[17] 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 $\sim 150\text{-cm}^{-1}$ band and the appearance of the broad peak at $\sim 280\ \mathrm{cm}^{-1}$ 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 narrowband and a broadband.[11,17] One cannot exclude also the possibility that spin stripes are formed, which break the spin-rotational and time-reversal invariance[16] and coexist with a charge order.[18]

CONCLUSIONS

In this work it is shown that the A_g mode at $\sim 100\ \mathrm{cm}^{-1}$ shows a classical soft-mode behavior even for high Sr-doped compounds (up to $x=0.17$), supporting its correlation with the LTO$\rightarrow$HTT transition for the Sr contents studied. Also, the mode at $\sim 270\ \mathrm{cm}^{-1}$ of A_g 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 $370\ \mathrm{cm}^{-1}$ that appear in the *xx-yy* polarization spectra are related to a symmetry breaking that occurs at temperatures that scale with T_c. The first band splits into 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 broadband was observed in the *xx-yy* polarization spectra at $\sim 280\ \mathrm{cm}^{-1}$, 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 $370\ \mathrm{cm}^{-1}$ 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 $\sim 280\text{-cm}^{-1}$ 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.

ACKNOWLEDGMENTS

The team from NTUA expresses its appreciation to the Greek Ministry of Education for financial support through the project Pythagoras I, cofunded by the European Social Fund (75%) and Greek National Resources (25%). C.P. and the work in Cambridge were supported by the Royal Society. We thank J. Cooper for providing some of the samples studied. Critical remarks by D. Mihailovic are also appreciated.

[1] B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, and G. Shirane, Phys. Rev. B **46**, 14034 (1992).

[2] S. Sugai, Phys. Rev. B **39**, 4306 (1989); S. Sugai *et al.*, Solid State Commun. **76**, 371 (1990).

[3] W. H. Weber, C. R. Peters, and E. M. Logothetis, J. Opt. Soc. Am. B **6**, 455 (1989).

[4] G. Burns, G. V. Chandrashekhar, F. H. Dacol, and M. W. Shafer, Solid State Commun. **68**, 67 (1988).

[5] R. J. Birgeneau, C. Y. Chen, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. Thio, T. R. Thurston, H. L. Tuller, J. D. Axe, P. Boni, and G. Shirane, Phys. Rev. Lett. **59**, 1329 (1987).

[6] D. Lampakis, D. Palles, E. Liarokapis, C. Panagopoulos, J. R. Cooper, H. Ehrenberg, and T. Hartmann, Phys. Rev. B **62**, 8811 (2000).

[7] A. V. Bazhenov, C. B. Rezchikov, and I. S. Smirnova, Physica C **273**, 9 (1996).

[8] A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito, Phys. Rev. Lett. **76**, 3412 (1996).

[9] P. G. Radaelli, D. G. Hinks, A. W. Mitchell, B. A. Hunter, J. L. Wagner, B. Dabrowski, K. G. Vandervoort, H. K. Viswanathan, and J. D. Jorgensen, Phys. Rev. B **49**, 4163 (1994).

[10] W. J. Padilla, M. Dumm, S. Komiya, Y. Ando, and D. N. Basov, Phys. Rev. B **72**, 205101 (2005).

[11] G. Blumberg, M. V. Klein, and S. W. Cheong, Phys. Rev. Lett. **80**, 564 (1998).

[12] L. Pintschovius and W. Reichardt, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1994), Vol. IV.
[13] R. T. Collins, Z. Schlesinger, G. V. Chandrashekhar, and M. W. Shafer, Phys. Rev. B **39**, 2251 (1989).
[14] R. J. McQueeney, J. L. Sarrao, P. G. Pagliuso, P. W. Stephens, and R. Osborn, Phys. Rev. Lett. **87**, 077001 (2001).
[15] R. J. McQueeney, J. L. Sarrao, and R. Osborn, Phys. Rev. B **60**, 80 (1999).
[16] S. A. Kivelson, I. P. Bindloss, E. Fradkin, V. Oganesyan, J. M. Tranquada, A. Kapitulnik, and C. Howard, Rev. Mod. Phys. **75**, 1201 (2003).
[17] V. V. Kabanov and D. Mihailovic, Phys. Rev. B **65**, 212508 (2002).
[18] O. Zachar, S. A. Kivelson, and V. J. Emery, Phys. Rev. B **57**, 1422 (1998).