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Abstract
Systematic Raman studies on several cuprates (YBa$_2$Cu$_3$O$_x$, YBa$_2$Cu$_4$O$_8$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$) have shown that at optimal doping the compounds are at the edge of lattice instability; once this level is exceeded, by means of doping or applying external hydrostatic pressure, the changes in the transition temperature are accompanied by spectral modifications. There are strong indications that the reduction in T_c is correlated with a separation into nanoscale phases, which involve the oxygen atoms of the CuO$_2$ planes. In this work, modifications with doping in the Raman spectra of the La$_{2-x}$Sr$_x$CuO$_4$ compound are presented, which show that spin or charge ordering is coupled with lattice distortions throughout the whole doping region.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

More than two decades after the discovery of high temperature superconductors (HTSCs) [1] the role of the lattice in the pairing mechanism of those compounds is still unclear, with many conflicting experiments. Raman spectroscopy is a powerful technique that can provide direct evidence about small lattice distortions. Although it probes only the $q \approx 0$ phonons in the Brillouin zone, due to its extreme sensitivity, it can detect a weak interaction of the lattice with the carriers or even the spin ordering. In several cuprates (YBa$_2$Cu$_3$O$_x$, YBa$_2$Cu$_4$O$_8$, and Bi$_2$Sr$_2$CaCu$_2$O$_8$) it was found that at optimal doping the compounds are at the edge of lattice instability; once this level is exceeded, by means of doping or applying external hydrostatic pressure, the T_c reduction is accompanied by spectral modifications in the phonons that involve in-phase vibrations of the plane oxygen (O$_{pl}$) atoms [3, 4]. This mode softens suddenly above optimal doping or it appears as a double peak under hydrostatic pressures [3, 4]. By slightly tilting the polarization axis, it has been shown that the relative intensity of the two peaks varies, clearly indicating that the new peak corresponds to a tilting of the octahedra [4]. This behavior seems to be quite general in all cuprates studied up to

now and it was attributed to a (nano)scale phase separation of a compound that seems to be close to an instability.

Another typical example of the cuprate superconducting family that shows a variety of phases with doping and temperature [2, 5] is La$_{2-x}$Sr$_x$CuO$_4$. This compound displays a characteristic soft mode at ≈ 120 cm^{-1} (for $x = 0$), that has the A$_g$ symmetry and is attributed to the tilting vibrations of the CuO$_6$ octahedra about the diagonal (110) axis [6, 7]. The mode is activated in the low temperature orthorhombic (LTO) phase, disappearing as we approach the high temperature tetragonal (HTT) more symmetric phase [6–8]. Of the rest of the Raman active phonons, the two strong modes are of A$_g$ symmetry and are attributed to the vibrations of the La/Sr and the apex oxygen atoms along the c axis [6, 7]. Other weaker modes appear upon Sr doping mostly at low temperatures and for doping levels for which the compound is superconducting. The peculiar characteristics of the soft mode and the origin of the weaker ones will be examined below.

2. Experimental details

Individual microcrystallites from a selected series of high quality La$_{2-x}$Sr$_x$Cu^{16,18}O$_4$ (85% substitution of ^{16}O by ^{18}O)

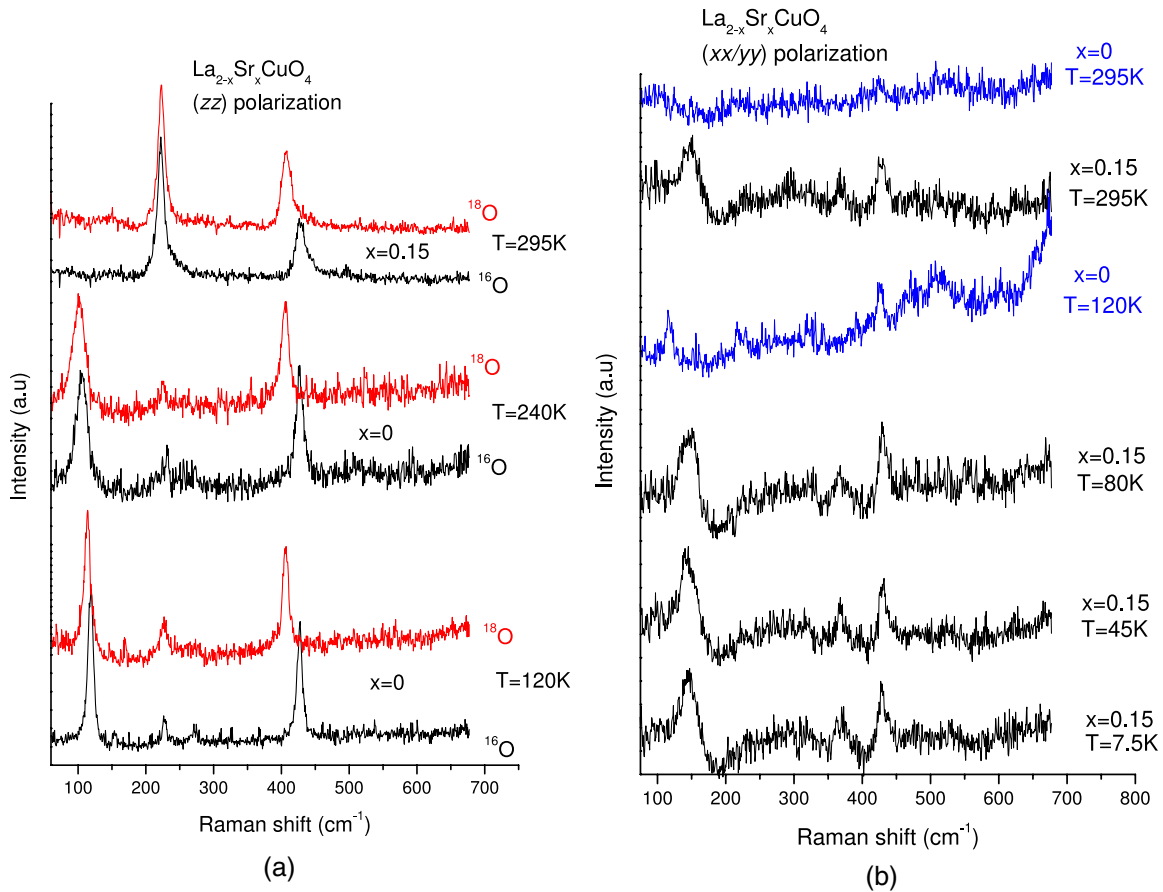**Figure 1.** (a) Typical spectra for selected temperatures and doping levels of the $La_{2-x}Sr_xCu^{16,18}O_4$ compounds in the *zz* polarization. (b) Typical spectra for selected temperatures of the $La_{1.85}Sr_{0.15}Cu^{16}O_4$ compound in the *xx* polarization.

polycrystalline compounds, with Sr doping in the range $0.00 \leqslant x \leqslant 0.3$, have been studied in the 7.5–350 K temperature region using Raman spectroscopy. The Raman spectra were obtained in the approximate $y(zz)y$ and $y(xx)y$ (or $x(yy)x$) scattering configurations or a mixture of them as the x and y axes could not be discriminated in the twinned samples. The triple spectrometer Jobin-Yvon T64000 was used, which is equipped with a liquid-nitrogen-cooled charge coupled device (CCD) and a microscope ($100\times$ magnification). Low temperatures were achieved by using an open-cycle Oxford cryostat operating either with liquid nitrogen or liquid helium. The 514.5 nm wavelength of an Ar^+ laser was used for excitation at a power level of 0.05–0.1 mW μm^{-2}. It appeared that the polycrystalline samples under vacuum were very sensitive to the local heating and special care was necessary to ensure that the laser power will be low enough to avoid any local heating during the many hours of measurements. On the basis of the soft mode energy and width we have estimated that the local heating of the sample due to the laser beam was less than 10 K. As a result, accumulation times for each measurement were of the order of 4–5 h.

3. Results and discussion

Typical Raman spectra of the LSCO compound for selected dopings and temperatures for the parallel polarizations of the

incoming and scattering light along the *c* axis (*zz* spectra) and the *ab* planes (*xx* spectra) are presented in figures 1(a) and (b) respectively. The data from two oxygen isotopes (^{16}O and ^{18}O) are presented in order to identify the modes related to vibrations of the oxygen atoms.

In figure 1(a), all five A_g phonons can be seen. Three of these, the La/Sr, the apex oxygen, and the weak mode at ≈ 273 cm^{-1}, involve ion vibrations along the *c* axis and the rest of the Raman active modes (the soft mode and the other very weak mode at ≈ 156 cm^{-1}) are attributed to the tilting vibrations of the octahedra [7]. The energy of the soft mode decreases and its width increases rapidly with increasing temperature as expected [6]. In the ranges $T = 285$–305 K for $x = 0.0$ and 77–100 K for $x = 0.015$ both energy and width show an abnormal behavior (figures 2(a) and (b) respectively). In this region, the energy of the soft mode remains constant and independent of temperature, while the width increases substantially. With the further increase in temperature the energy of the soft mode decreases again. The effect in the La_2CuO_4 compound (figure 2(a)) is much more pronounced and it occurs at higher temperatures than for the other Sr concentration (figure 2(b)). The results from the oxygen isotopic substituted compounds show that there is no isotope effect on the temperature ranges where this abnormal behavior is observed.

According to the phase diagram of LSCO (figure 3), the structural LTO $\rightarrow$ HTT transition temperature for the
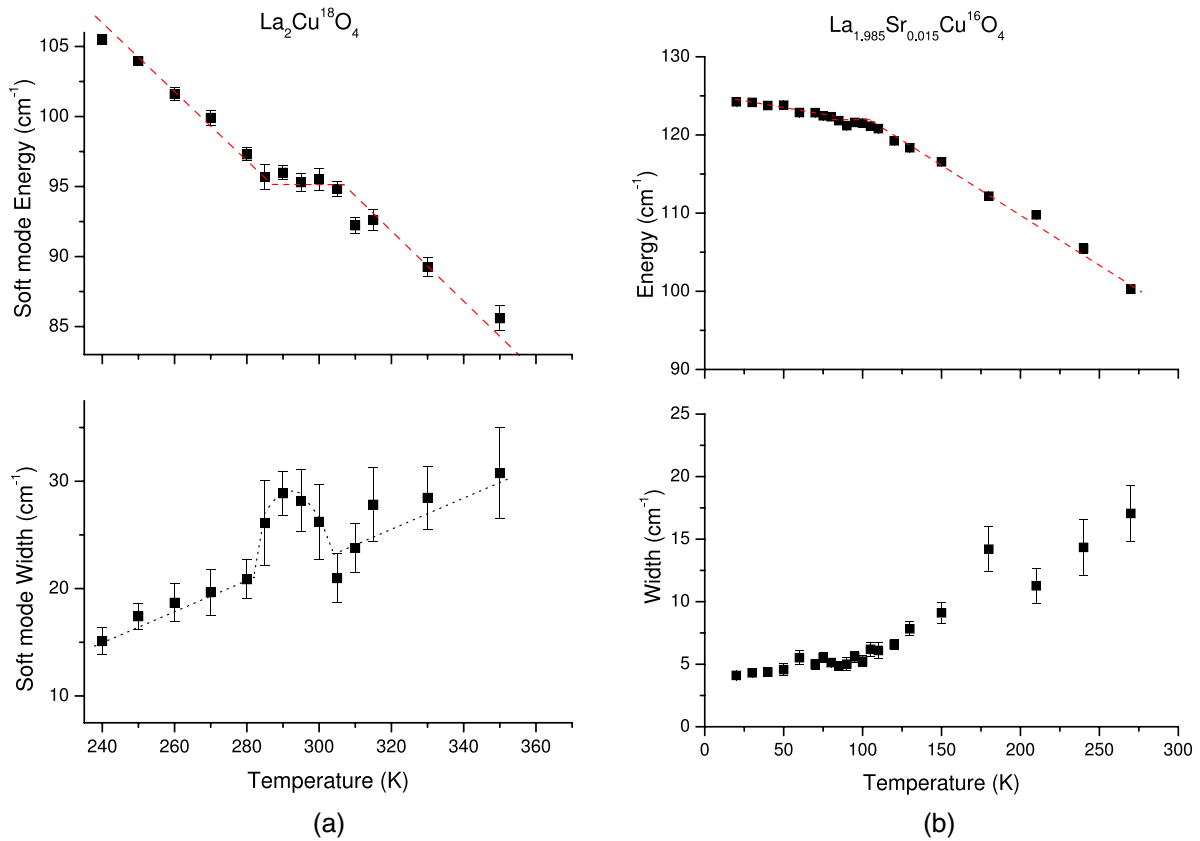
Figure 2. (a) The temperature dependence of the energy and width of the soft mode for the $La_2Cu^{18}O_4$ compound. (b) The temperature dependence of the energy and width of the soft mode for the $La_{1.985}Sr_{0.015}Cu^{16}O_4$ compound.
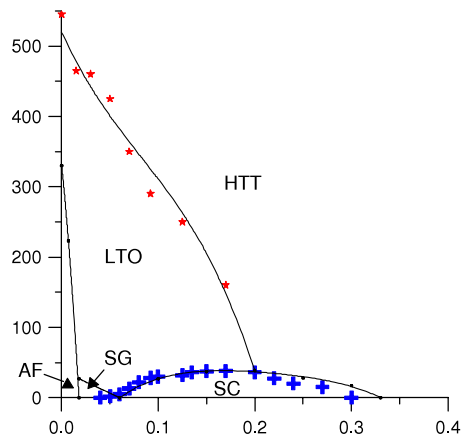

Figure 3. Phase diagram of LSCO. Daggers and stars indicate experimental data points.

insulating La_2CuO_4 sample is expected at ≈ 560 K and cannot be related to the abnormal behavior observed in the range $T = 285$–305 K. As figure 3 schematically shows, close to room temperature there is a Néel transition to the antiferromagnetic phase [2, 9] for $x = 0.0$, while for $x = 0.015$ the Néel temperature is less than 100 K, falling to zero for $x \approx 0.02$ [2]. Both temperatures agree with the ranges where the abnormal behavior of the soft mode was observed for the two concentrations. Besides, the Néel temperature is not affected

by the oxygen isotopic substitution [10] and therefore any effect related to the spin ordering should be independent of the isotopic substitution. The data in figure 2 seem to support the idea that the effects observed at $T = 285$–305 K for $x = 0$ and 77–100 K for $x = 0.015$ are mostly related to the antiferromagnetic (AF) ordering. The present data provide strong evidence for the coupling of the antiferromagnetic ordering with the lattice at least for the low doping levels. Such magnetoelastic coupling between spin ordering and the lattice (octahedra of the oxygen atoms) has been proposed in [11]. Here there is a clear proof that the tilting (soft) mode of the octahedra is affected by the spin ordering. With increasing doping the LTO $\rightarrow$ HTT structural phase transition temperature decreases, to disappear for $x \simeq 0.22$. The soft mode will also disappear at this doping level. On the other hand, the AF ordering exists only for low doping levels. It is therefore interesting to investigate the coupling of the soft mode over the whole doping region. Our data indicate that there is no such anomaly for higher Sr concentrations, supporting our assumption that the effect observed (figure 2) is due to the coupling of the lattice (tilting of the octahedra) with the spin ordering.

In the $y(xx)y$ (or $x(yy)x$) polarization Raman spectra (figure 1(b)), additionally to the A_g symmetry phonons at ≈ 229 cm^{-1} for the La/Sr ions and at ≈ 429 cm^{-1} for the apical oxygen, certain new bands at ≈ 150, ≈ 280, and ≈ 370 cm^{-1} appear mainly at low temperatures and in the superconducting
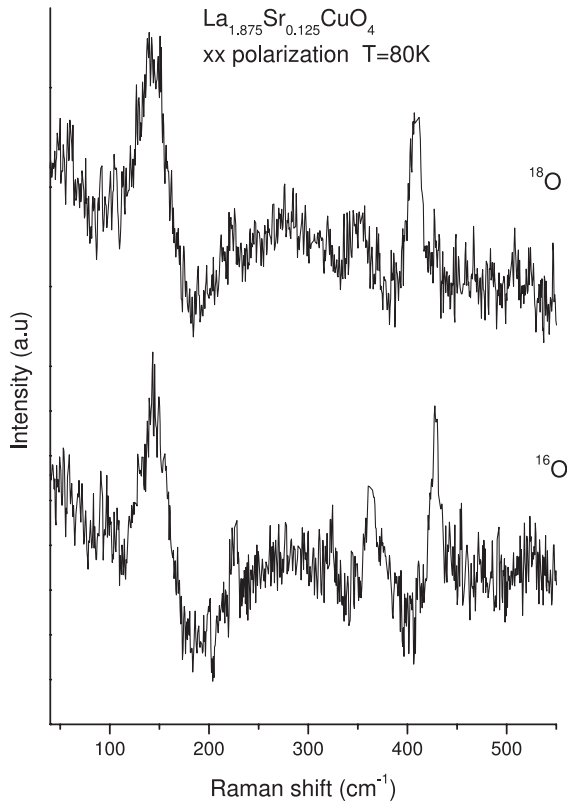
Figure 4. Raman spectra for the parallel polarizations of the two oxygen isotopes of the La$_{1.875}$Sr$_{0.125}$CuO$_4$ compound.

doping region $0.03 < x < 0.27$. All bands, including the new ones, disappear in the crossed polarization and therefore they approximately have the A$_1$ symmetry. This apparent symmetry excludes the possibility for the three new bands to be associated with the B$_{1g}$, B$_{2g}$, and B$_{3g}$ Raman active phonons. The study of the effect of the oxygen isotopic substitution on the three new bands proves that the band at $\approx$150 cm^{-1} has an $\approx$(1.5$\pm$0.5)% energy shift, the band at $\approx$280 cm^{-1} an $\approx$(3.5$\pm$0.5)% energy shift, while the band at $\approx$370 cm^{-1} follows very well the mass harmonic law of a purely oxygen mode ($\approx$5.0%) (figure 4).

In previous works [6, 9, 12] the bands at $\approx$150 and $\approx$370 cm^{-1} have been attributed to the TO IR modes with eigenvectors along the CuO$_2$ planes, while there was no proposed association for the $\approx$280 cm^{-1} band. Even though we agree that the new bands which appear in the *xx* polarization Raman spectra are IR modes, on the basis of our experimental data from the oxygen isotopic substitution, we believe that the assignment given in the work of [6, 9, 12] is not correct. From the association of the D$_{2h}$ point group (for the orthorhombic phase) with its subgroups [13] one can find that with the loss of inversion symmetry (which is necessary for IR modes to become Raman active), the B$_{1u}$, B$_{2u}$, B$_{3u}$, and A$_u$ phonons of D$_{2h}$ are associated with the A$_1$ symmetry modes of the C$_z^{2v}$, C$_y^{2v}$, C$_x^{2v}$, and D$_2$ subgroups respectively. Comparing the observed peaks with those for IR active phonons of similar energy [14] and concerning the results from the oxygen isotopic substitution, certain possibilities are revealed. The band at $\approx$150 cm^{-1} can be related to the following IR modes: the B$_{3u}$ of La/Sr (following the *Abma* notation of the

orthorhombic phase), the B$_{1u}$ of Cu$_{pl}$, the B$_{1u}$ or the silent A$_u$ of the La/Sr atoms and finally the B$_{2u}$ of the O$_{ab}$ with a mixture of Cu and La/Sr atoms. The wide band at $\approx$280 cm^{-1} with one of the four phonons; the B$_{1u}$ symmetry of O$_{apex}$ and O$_{ab}$, the silent A$_u$ of the O$_{ab}$ atoms and the B$_{3u}$ phonon of the Cu$_{pl}$ or of the Cu with a mixture of La/Sr and O$_{ab}$ atoms, and finally, the $\approx$370 cm^{-1} with the B$_{3u}$ phonon of the O$_{apex}$.

It is quite possible that the $\approx$150 and $\approx$280 cm^{-1} peaks are composite bands consisting of several modes, as our assignment has shown. In fact, the band at $\approx$150 cm^{-1} appears in certain concentrations and temperatures as multiple (two or three) peaks. Similarly, the $\approx$280 cm^{-1} band is very wide (figure 1(b)) to be considered as a single mode. Besides, in the compounds with oxygen isotopic substitution, the $\approx$280 cm^{-1} band appears with a modified width, which could not happen unless it was consisting of multiple modes, some of them related (and shifting) with vibrations of the oxygen atoms and others involving motion of the Cu$_{pl}$ or the La/Sr atoms.

Since the IR modes appear in the Raman spectra for those doping levels where the compound becomes superconducting and mainly at low temperatures, it is important to investigate possible reasons for the inversion symmetry breaking. Any connection of the effect with the orthorhombic to tetragonal phase transition can be excluded, because there are no IR modes at ambient temperature in the pure La$_2$CuO$_4$ compound, which is orthorhombic. The modes appear with Sr doping and increase in intensity, showing a maximum around optimal doping and disappear in the overdoped region. One could attribute them to the disorder introduced by the Sr substitution. Such an effect should increase gradually with the amount of Sr and not disappear with $x \approx 0.25$ as for the IR modes. Other $q \cong 0$ Raman active modes can be also excluded, since the new modes persist even in the tetragonal phase, where very few phonons can be observed. One cannot exclude phonons from the edges of the Brillouin zone. Such a mode will indicate the formation of superstructures along some direction, which could be the case. The other possibility is just the breaking of the local inversion symmetry. This can happen from the formation of stripes or polarons. Stripes will probably induce a superstructure, so this could also activate phonons from other high symmetry points of the Brillouin zone. The formation of polarons or stripes could justify the connection of the new modes and the inversion symmetry breaking with the appearance of superconductivity.

4. Conclusions

For several cuprates, modifications in the Raman spectra with chemical doping (or pressure) have been observed, with new modes appearing or others split. These changes are correlated with modifications in T_c and point to a separation and coexistence of phases. For La$_{2-x}$Sr$_x$CuO$_4$ modifications have been observed in the soft mode energy for very low doping levels for temperatures that coincide with the antiferromagnetic ordering. In this way, the soft mode seems to be coupled with spin ordering. Besides, new modes appear at doping levels where the compound is superconducting at temperatures above T_c apparently from a local symmetry breaking of the lattice.

These changes can be attributed to the formation of stripes or polarons, that reduce the local symmetry and are related to the superconductivity.

Acknowledgments

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