Raman spectroscopic evidence of lattice effects across the phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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Abstract. The doping and temperature dependence of the Raman spectra of high-quality $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ polycrystalline compounds with $x=0.0-0.3$ have been investigated. The spectral characteristics of the soft phonon that appears in the ($zz$) polarization spectra of the LTO phase show an abnormal behaviour close to Néel transition temperature for $x=0.0$ (in the temperature range 285-305K) and for $x=0.015$ (in the range 77-100K), indicating an apparent coupling of the lattice to the spin ordering. The isotopic shift of the soft mode deviates from the mass harmonic law at all temperatures and this deviation increases substantially for $T>175$K towards room temperature. In the other scattering polarization ($xx$ or $yy$), certain new bands at $\sim$150 cm$^{-1}$, $\sim$280 cm$^{-1}$, and $\sim$370 cm$^{-1}$ appear mainly at low temperatures and in the superconducting doping region $0.03<x<0.27$. From the study of the effects of the oxygen isotopic substitution, the possible reduction of symmetry, the doping, and the temperature dependence, the new modes have been assigned to specific IR phonons, which are activated in the Raman spectra from the local breaking of the inversion symmetry.

1. Introduction

The discovery [1] of high–$T_C$ superconductors have led to a plethora of experimental and theoretical studies on these systems. The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) compound shows upon doping and temperature a variety of phases (Fig.1) including superconductivity [2]. One of the main conclusions from the Raman investigations of the vibrational modes of LSCO has been the existence of a soft mode at $\sim$100 cm$^{-1}$ of $A_g$ symmetry, attributed to the tilting vibrations of the CuO$_6$ octahedra about the diagonal (110) axis. This mode is activated by the High Temperature Tetragonal (HTT) to Low Temperature Orthorhombic (LTO) structural phase transition [3–5]. The substitution of $^{16}$O by the heavier $^{18}$O is expected to decrease the energy of the oxygen phonons, including the soft mode, due to the mass difference. Therefore it can provide important evidence on the possible anharmonic
effects in the LSCO compounds [6]. Furthermore, it can help characterize the symmetry forbidden phonons at ~150 cm$^{-1}$, ~280 cm$^{-1}$, and ~370 cm$^{-1}$, which appear in the $\gamma_{(xx)} \gamma$ polarization Raman spectra, mainly at low temperatures and in the superconducting doping region $0.03<x<0.27$ [3, 7-10].

In the present work, the oxygen isotopic substitution, the doping, and the temperature dependence of the soft mode are investigated in order to examine in detail the behaviour of the soft mode at low temperatures expected to show strong anharmonicity. In addition, the symmetry and the oxygen isotopic effect on the new modes is examined to delineate their origin.

2. Experimental setup

Polycrystalline compounds of nominal La$_{2-x}$Sr$_x$Cu$_{16.18}$O$_4$ (85% substitution $^{16}$O by $^{18}$O) with $x=0.0$-$0.3$ have been prepared by the solid state reaction technique and examined using Raman spectroscopy. The Raman spectra were obtained at nominal temperatures 20-350K with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid nitrogen cooled charged coupled device (CCD) and a microscope (magnification $\times$100). The 514.5 nm line of an Ar$^+$ laser was used for excitation. Low temperature measurements were achieved using an open-cycle Oxford cryostat appropriately modified to allow the study of microcrystallites at various scattering geometries. Spectra were obtained on individual microcrystals (typical size of a few µm) in the approximate $\gamma_{(zz)} \gamma$ and $\gamma_{(xx)} \gamma$ (or $\gamma_{(yy)} \gamma$) scattering configurations. In order to avoid sample heating at the laser spot, very low laser power densities were necessary and the local heating of the sample was estimated to be less than 10K, as induced from the energy shift and the width of the very sensitive to temperature soft mode. As a result, accumulation times were of the order of 3-12 hours.

![Figure 2](image.png)

**Figure 2.** Typical Raman spectra in the approximate $\gamma_{(zz)} \gamma$ polarization of (a) La$_2$Cu$^{18}$O$_4$ and (b) La$_{1.985}$Sr$_{0.015}$Cu$^{16}$O$_4$. 
3. Results and discussion

Raman spectra for selected temperatures of pure La$_2$Cu$_{18}$O$_4$ and of the doped compound with $x=0.015$, for the parallel polarizations of the incoming and scattering light along the c-axis ($zz$ spectra) are presented in Figures 2a and 2b respectively. In both cases, all five $A_g$ phonons have been detected. Three of these, the La/Sr, the apex oxygen, and the weak mode at $\sim 273$ 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 $\sim 156$ cm$^{-1}$) are attributed to the tilting vibrations of the octaedra.

It is clear that the soft mode is strongly damped with increasing temperature and doping, while its width increases (Fig.3). The extrapolation to zero of the soft mode squared energy defines the LTO$\rightarrow$HTT transition temperature (Fig.1, red stars). An anomaly at 50-70K for $x=0.092$-0.125 has also been observed. Additionally, in the temperature range $T=285$-295K for La$_2$Cu$_{18}$O$_4$ the soft mode becomes much wider. Similar behavior is observed for the other isotope and the combined data for the isotopic shift as well as the energy and the width of the soft mode are presented in Figures 4 and 5 respectively.

From the amount of isotopic substitution one can induce that the apical oxygen phonon follows quite well the mass harmonic law independently of temperature. On the other hand, the soft mode clearly deviates from the harmonic law especially for $T>175$K (Fig.4). Furthermore, in the temperature range $T=285$-305K the energy of the soft mode remains constant and independent of temperature for both oxygen isotopes, while the width increases substantially (Fig.5a).

![Figure 3. Temperature dependence of soft mode width (top) and squared energy (bottom) for various Sr concentrations.](image)

![Figure 4. The relative shift of the soft mode and the apex oxygen mode energies due to the oxygen isotopic substitution in the compound La$_2$Cu$_{18}$O$_4$.](image)
The apex oxygen phonon shows some fluctuations both in energy and width in the same temperature region (Fig.5b), but their temperature dependence is much weaker than for the soft mode, and any related effect cannot be clearly established. With the further increase in temperature the energy of the soft mode decreases again following the trend that exists for T<280K (Fig.5a). For the doped compound La$_{1.985}$Sr$_{0.015}$Cu$_{16}$O$_4$ the soft mode anomaly (independence of temperature) appears in the range T=77-100K (Fig.6).

**Figure 5.** The temperature dependence of the energy and width of (a) the soft mode and (b) the apex oxygen mode for the La$_2$CuO$_4$ compound.

**Figure 6.** Temperature dependence of the energy and width of the soft mode for La$_{1.985}$Sr$_{0.015}$Cu$_{16}$O$_4$. 
The extrapolation of the oxygen isotope shift of the soft mode points, as expected, to the Orthorhombic to Tetragonal phase transition temperature (Fig.4) and provides another method of defining it (Fig.1). The decreasing of the isotopic shift with increasing temperature is a characteristic of the anharmonicity of this mode. The temperature at ~175K for which the x=0.0 compound approaches its low temperature asymptotic value cannot be related with the Debye temperature [11]. On the other hand, the difference in the isotopic shift between apex and soft mode at low temperatures is attributed to the local heating at the laser spot and it can be a measure of the local temperature rise.

According to the phase diagram of LSCO (Fig.1), the structural LTO→HTT transition temperature, for the insulating La2CuO4 sample is ~560K and cannot be related with the abnormal behaviour observed in the range T=285-305K. As Fig.1 schematically shows, close to room temperature there is a Néel transition to the antiferromagnetic phase [2, 12] for x=0.0, while for x=0.015 the Néel temperature is less than 100K falling to zero for x=0.02 [2]. The Néel temperature is not affected by the oxygen isotopic substitution [13] and therefore any effect related with the spin ordering should be independent of the isotopic substitution. The data in Fig.5a seems to support the idea that the effects observed at T=285-305K are mostly related with the antiferromagnetic (AF) ordering. The rich phase diagram of the LSCO compounds indicates that the system is governed by several competing ordering parameters. The present data provide strong evidence for the coupling of the antiferromagnetic ordering with the lattice at least for the low doping levels. Since the soft mode is associated with the tilting vibrations of the apex oxygen, the coupling of the AF state with the lattice must be related with the changes in the tilting angle induced from the AF ordering in the CuO2 planes. These results can explain the small fluctuations observed in the spectral characteristics of the apex oxygen phonon of Ag-symmetry with the antiferromagnetic ordering (Fig.5b).

In a recent work, Goto et.al [14] observed a significant change in the NMR peak splitting pattern below 50K for LSCO (x=0.12), indicating an evolution of a local structure with the buckling pattern along (100) in CuO2 plane. According to the authors this buckling must be static and with extremely short coherence length, since no evidence for a macroscopic structural transformation has been observed [15]. In our data there is a certain anomaly in energy and width of the soft mode at about the same temperature (50-70K) for x=0.092-0.125 (indicated by an arrow in Fig.3), which requires further investigation.

In the y(xx) and x(yy) polarization Raman spectra additionally to the Ag-symmetry phonons at ~229 cm⁻¹ of the La/Sr ions and at ~429 cm⁻¹ of the apical oxygen, new bands at ~150 cm⁻¹, ~280 cm⁻¹ and ~370 cm⁻¹ appear mainly at low temperatures and in the superconducting doping region 0.03<x<0.27 (Fig.7). No change in the spectral characteristics of the Ag modes or the new bands has been observed across Tc. All bands, including the new ones, disappear in the crossed polarization (Fig.8a) and therefore have the A1- symmetry. This apparent symmetry excludes the possibility for the three new bands to be associated with the B1g, B2g, and B3g Raman active phonons. The study of the effect of the oxygen isotopic substitution on the three new bands proves that the band at ~150 cm⁻¹ has a ~1.5±0.5)% energy shift, the band at ~280 cm⁻¹ a ~3.5±0.5)% energy shift, while the band at ~370 cm⁻¹ follows very well the mass harmonic law of a purely oxygen mode (~5.0%) (Fig.8b).

In previous works [7, 8, 16] the same bands at ~150 cm⁻¹, ~280 cm⁻¹, and ~370 cm⁻¹ have also been detected. According to Neto [16] the bands at ~150 cm⁻¹ and ~280 cm⁻¹ are the Ag-symmetry phonons of similar energy. As Sr doping increases many more peaks can be observed from the formation of superstructures and the enlargement of the atomic unit cell. Actually, the Ag phonons that have been suggested usually appear in the (zz) polarization Raman spectra and in slightly different energies (~156 cm⁻¹ and ~273 cm⁻¹). Furthermore, the ~370 cm⁻¹ band cannot be assigned with this assumption and the results from the oxygen isotopic substitution do not agree with the association of the almost unshifted band at ~150 cm⁻¹ to the band at ~156 cm⁻¹ with ~4.0% energy shift.

In the work of Sugai et.al [7, 8] the bands at ~150 cm⁻¹ and ~370 cm⁻¹ have been attributed to the TO IR modes with eigenvectors along the CuO2 planes, while there was no proposed association for the ~280 cm⁻¹ band. Based on our experimental data from the oxygen isotopic substitution, we believe that the assignment given in the work of Refs. [7, 8] is not correct.
From the association of the $D_{2h}$ point group (for the orthorhombic phase) with its subgroups [17] 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 $C_{2v}$, $C_{2}'$, $C_{2}'$, and $D_{2}$ subgroups respectively. Comparing the observed peaks with IR-active phonons of similar energy [18] and concerning the results from the oxygen isotopic substitution certain possibilities are revealed. The band at $\sim$150 cm$^{-1}$ can be related with 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 $\sim$280 cm$^{-1}$ with one of the four phonons; the $B_{1u}$-symmetry of O$_{pec}$ 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. Finally, the $\sim$370 cm$^{-1}$ with the $B_{2u}$ phonon of the O$_{pec}$.

At low temperatures the band at $\sim$150 cm$^{-1}$ undergoes a spectral modification and appears as a double peak, a wide one at $\sim$120 cm$^{-1}$, a narrower one at $\sim$150 cm$^{-1}$ and at low Sr concentrations as a triple peak with the additional contribution of a peak at $\sim$170 cm$^{-1}$ [9]. The energy and width of the $\sim$120 cm$^{-1}$ peak increase with doping (Fig.9a), which denote that it can be correlated with the La/Sr vibrations of $B_{3u}$, $B_{1u}$ or $A_{u}$ symmetry. The small isotopic shift of the narrow peak at $\sim$150 cm$^{-1}$ and its unchanged energy with increasing doping indicate that this band can be associated with the vibrations of the Cu with a mixture of O atoms (B$_{1u}$ or B$_{2u}$ symmetry). The band at $\sim$370 cm$^{-1}$ can be related with only one IR phonon and to oxygen atoms, vibrating perpendicular to the CuO$_2$ planes. The $\sim$280 cm$^{-1}$ band must be related to a mixture of four IR phonons, three of which involve vibrations along the c-
axis and the fourth one along the ab planes. Concerning the isotopic shift of this band (~3.5±0.5%) we conclude that it cannot be assigned to only the B_{3u} symmetry phonon of the Cu vibrating along the planes, which is expected to have smaller isotopic shift. Furthermore, this band changes its shape and reduces its width with the oxygen isotopic substitution (Fig.8b). This could not occur, unless it is composed of several modes, some shifting with the isotopic substitution and others being unaffected.

Figure 9. (a) Temperature dependence of the energy and width for the two peaks at ~120 cm\(^{-1}\) and ~150 cm\(^{-1}\) of the low energy new bands (measured at 10K), (b) Temperature and doping dependence of the relative intensities to the apical oxygen of the bands at ~150 cm\(^{-1}\) and ~370 cm\(^{-1}\).

Concerning the reason of the inversion symmetry breaking, one could assign it to the Sr substitution for La. In such a case, the intensity of the IR modes activated in the Raman spectra would be expected to increase with doping, and this is certainly not the case here since the intensity of the new modes is gradually reduced above optimal doping (Fig.9b). Another possibility is the new bands to be related with the Orthorhombic to Tetragonal phase transition, but it is clear that, even though the band at ~370 cm\(^{-1}\) gradually looses strength with increasing temperature, it is present even in the tetragonal phase at room temperature (Figs.7, 8).

Another possible origin of the breaking of the inversion symmetry may be the uneven electric field that exists across the CuO\(_2\) planes. The electric field coexists and interacts with the carriers introduced with doping, which causes the usual buckling effect in the CuO\(_2\) planes and the creation of local strains that could drive the formation of stripes or other structures including phase separation. These local lattice distortions are frozen at low temperatures and can become detectable by Raman spectroscopy.
4. Conclusions
In this work it is shown that the energy of the soft mode remains constant and independent of temperature in the temperature range 285-305K, for $x=0.0$ and 77-100K for $x=0.015$, which are roughly the Néel temperatures for the corresponding compounds. This is a strong indication of the AF coupling with the lattice. In addition, we have studied systematically the appearance of symmetry forbidden modes in the Raman spectra and suggested an assignment based on their dependence on doping, temperature, and oxygen isotope substitution. All three bands have been attributed to IR modes with eigenvectors not only within the ab-planes but also along the c-axis.

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