Doping and temperature dependence of inversion symmetry breaking in \(\text{La}_2\text{Sr}_x\text{CuO}_4\)

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**Abstract**

The doping dependence of the Raman spectra of high quality \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) polycrystalline compounds has been investigated at low temperatures. It is shown that symmetry forbidden bands peaked at \(\sim 150\ \text{cm}^{-1}\), \(\sim 280\ \text{cm}^{-1}\), and \(\sim 370\ \text{cm}^{-1}\) are activated in the \((xx/yy)\) polarization Raman spectra due to the local breaking of the inversion symmetry mainly at low temperatures and for doping concentrations for which the compound is superconducting. The apparent \(A_1\) character of the activated modes in the symmetry reduced phase indicates a reduction from the \(D_{2h}\) to \(C_{2v}\) or \(D_2\) crystal symmetries, which associates the observed modes to specific IR-active phonons with eigenvectors mainly along the \(c\)-axis. The temperature and doping dependence of this inversion symmetry breaking and the superconducting transition temperature are very similar, though the symmetry reduction occurs at significantly higher temperatures.

1. Introduction

One of the puzzles in the cuprates concerns their rich phase diagram and the role of the lattice in the pairing mechanism. Among other techniques, Raman spectroscopy can provide direct evidence about small lattice distortions and therefore detect a possible weak interaction of the lattice with the charge or spin ordering, although it probes only the interaction of the lattice with the charge or spin ordering, although it cannot be assigned to any apparent structural changes of the system, it might originate from a charge redistribution, which occurs at temperatures above \(T_c\) and affects the electronic states and the polarizabilities of the relative atoms at certain critical Sr concentrations. Furthermore, symmetry forbidden phonons at \(\sim 150\ \text{cm}^{-1}\) and \(\sim 370\ \text{cm}^{-1}\) appeared in the \((xx/yy)\) polarization Raman spectra and at low temperatures a broad peak at \(\sim 280\ \text{cm}^{-1}\) [6,7]. The intensity of these modes seems to have a maximum close to the optimal doping.

In the present work, the effect of the oxygen isotopic substitution, the symmetry, and the doping and temperature dependence of the new modes are investigated systematically in order to delineate their origin and the reason for its apparent correlation to superconductivity. We show that the assignment given up to now for the new modes is not correct and the effect of the inversion symmetry breaking may have a common origin with superconductivity, that could explain the correlation of the new modes with \(T_c\).

2. Experimental setup

The Raman spectra were obtained in the approximate \(y(zz)y\) and \(y(xx)y\) (or \(x(yy)x\)) scattering configurations from individual microcrystallites of a series of high quality \(\text{La}_2\text{Sr}_x\text{CuO}_4\).
3. Results

Raman spectra for selected temperatures for the La$_{2-x}$Sr$_x$CuO$_4$ compound with $x = 0.05$–0.24 are presented in Fig. 1 for the parallel polarizations of the incoming and scattered light along the ab plane (xx or yy spectra). In addition to the $A_g$-symmetry phonons of the La/Sr ions appearing at $\sim 229$ cm$^{-1}$ and of the apical oxygen at $\sim 429$ cm$^{-1}$, three, non predicted from symmetry, 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 $0.03 < x < 0.27$ (Fig. 1). In the other scattering polarization [zz], the soft mode and two weak narrow peaks (the other three $A_g$-symmetry phonons) at $\sim 156$ cm$^{-1}$ and $\sim 273$ cm$^{-1}$ have been detected [6]. Three of these $A_g$ phonons involve ion vibrations along the c-axis and the other two (the soft mode and the mode at $\sim 156$ cm$^{-1}$) are attributed to tilting vibrations of the octahedra. No change in the spectral characteristics of the $A_g$ modes or the new bands has been observed across $T_c$.

In the crossed polarization Raman spectra (Fig. 2a) none of the $A_g$ modes or the three new bands has been observed (the weak peaks appearing in this spectrum is a leakage from the parallel geometry). Therefore they all have the $A_g$-symmetry and as a result the three new bands cannot to be associated with the $B_{1g}, B_{2g}$ or $B_{3g}$ Raman-active phonons. Besides, in such a case we could not justify the presence of these peaks in only a certain doping and temperature region.

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 doping levels ($x \leq 0.07$) as a triple peak with the additional contribution of a weak peak at $\sim 170$ cm$^{-1}$ (Fig. 3) [6]. The deconvolution of the low energy region into subbands, indicates that the narrow peak at $\sim 150$ cm$^{-1}$ remains constant in energy independent of doping, while the wide component at $\sim 120$ cm$^{-1}$ is modified (Fig. 4). Besides, the width of those two constituents shows a characteristic modification with doping increasing almost linearly with the amount of Sr up to $x \approx 0.1$ and then it remains constant or slightly decreases (Fig. 4). Furthermore, the intensity of the band at $\sim 120$ cm$^{-1}$ diminishes around $x \approx 0.20$ and for higher Sr concentrations only the narrow peak at $\sim 150$ cm$^{-1}$ has been detected.

The calculated energy shift due to the oxygen isotopic substitution for the narrow peak at $\sim 150$ cm$^{-1}$ of the low energy band is $(1.5 \pm 0.5\%)$ (Fig. 2b), $\sim 5.0\%$ for the $\sim 370$ cm$^{-1}$ band which follows very well the mass harmonic law for a purely oxygen mode, while the isotopic shift for the $\sim 280$ cm$^{-1}$ broad band is somehow in the middle of the other two cases (Fig. 2b).

Similar bands at $\sim 150$ cm$^{-1}$, $\sim 280$ cm$^{-1}$, and $\sim 370$ cm$^{-1}$ have also been observed in previous works [3,8] and assigned either to IR modes with eigenvectors along the ab-plane [3] or to the $A_g$-symmetry phonons of similar energy that usually appear in the (zz)-scattering polarization [8]. The main difference of our experimental approach lies in the study of the new modes in the whole range of Sr doping combined with oxygen isotopic substitution that excludes several suggested possibilities, in connection with a...
systematic analysis of the expected $A_1$-character modes from a reduction of local symmetry. In the following, the various suggestions will be scrutinized in order to define the mechanism that can explain all data available.

4. Discussion

Recently, the appearance of the new bands has been attributed to $A_g$ phonons and the formation of a supermodulated structure from the magnetoelastic coupling between the spin (copper) configuration and the oxygen octahedra [8]. Actually the two suggested $A_g$ phonons appear in the $(zz)$-polarization and at slightly different energies ($\sim 156$ cm$^{-1}$ and $\sim 273$ cm$^{-1}$) from the $(xx)$-spectra wide bands. Besides, the almost unshifted mode at $\sim 150$ cm$^{-1}$ cannot be related with the $A_g$ Raman active phonon of similar energy ($\sim 156$ cm$^{-1}$) that involves vibrations of the oxygen atoms along the ab planes, which has an isotopic shift of $\sim (4.0 \pm 0.5)%$. Furthermore, the $\sim 370$ cm$^{-1}$ band cannot be assigned with this assumption.

Another possibility is the three bands to be assigned to zone-boundary phonons, activated by the formation of superlattice structures. The apparent $A_1$-symmetry of the new bands would be a consequence of the reduction of symmetry as one moves away from the $I$ point to the edge of the Brillouin zone. Since there are several phonons in the relative regions, such possibility cannot be excluded for those bands [9]. But, we should point out that the strong $A_g$-symmetry modes of the La/Sr and apical atoms do not show any sign of additional satellite peaks, which will confirm the doubling of the unit cell.

Concerning the origin of the wide band at $\sim 280$ cm$^{-1}$ (35 meV), one could assign it to a peak in the phonon density of states (PDS), since at optimal doped compound, close to half-filling, the Fermi surface passes through a van Hove singularity and the density of states has a maximum. Although, the absence of a wide peak around this energy in inelastic neutron scattering measurements [9,10] does not confirm this scenario. It should be pointed out that McQueeney et al. [10] have observed a peak at 70 meV ($\sim 560$ cm$^{-1}$) for $La_{1.85}Sr_{0.15}CuO_4$ and attributed it to a peak in the PDS as a van Hove singularity. This has twice the energy of the wide band at $\sim 280$ cm$^{-1}$ which is observed in our Raman measurements. On the other hand no peak in the phonon density of states around 35 meV ($\sim 280$ cm$^{-1}$) has been observed [9,10].

Additionally, there is a possibility that the origin of the $\sim 280$ cm$^{-1}$ band to be considered as electronic. Chen et al. [11] studied the low energy Raman continuum of a $x = 0.17$ LSCO single crystal in different scattering geometries and found that the electronic scattering contributes with two wide bands at $\sim 130$ cm$^{-1}$ and $\sim 200$ cm$^{-1}$ of $B_{2g}$ and $B_{1g}$ symmetry, respectively. Besides, they have observed the same wide bands with us at $\sim 150$ cm$^{-1}$ and $\sim 280$ cm$^{-1}$ in the $xx$ and $xx'$ scattering configurations. The $\sim 130$ cm$^{-1}$ electronic continuum which is close to the $\sim 150$ cm$^{-1}$ band, appears only in the superconducting state and therefore it is considered as the pair breaking peak in LSCO as observed from the $B_{2g}$ channel [11,12], while the $\sim 150$ cm$^{-1}$ band can be seen at both the superconducting and the normal state. Furthermore, the electronic continuum peak at $\sim 200$ cm$^{-1}$ appears also only for temperatures below $T_c$ and is far from the broad peak at $\sim 280$ cm$^{-1}$, which appears in the spectra till much higher temperatures. Since we work with polycrystalline compounds, it is difficult to separate the $xx$ and $yy$-axis, and therefore discriminate the $B_{1g}$ or $B_{2g}$ contributions in our Raman spectra. So, we cannot tell about the exact symmetry of the bands at $\sim 150$ cm$^{-1}$ and $\sim 280$ cm$^{-1}$, but we can certainly state that they are not of electronic origin.

In a previous work, two of the new bands ($\sim 150$ cm$^{-1}$ and $\sim 370$ cm$^{-1}$) had been attributed to the TO IR phonons of $B_{1u}$ and/or $B_{2g}$ symmetry with polarization vectors along the CuO$_2$...
planes, activated by the local breaking of the inversion symmetry [7]. No assignment was suggested for the ~280 cm⁻¹ wide band [7]. Although the author did not specify the origin of the B₁u and B₂u symmetry IR phonons, from the reference provided one can speculate that they concern the ab-plane vibrations of the La/Sr atoms with a mixture of Oapex and of the Cu and O atoms [13]. Our experimental results from the oxygen isotopic shift does not agree with the assignment given in this work (Fig. 2) [7]. Besides, it is not clear why the wide low energy band at ~150 cm⁻¹ consists of three peaks.

We suggest that all new bands and peaks can be associated with IR modes activated by the breaking of the inversion symmetry. This is an explanation that can match all our experimental findings. Recent IR data from high quality detwinned LSCO crystals show that bands of similar energy are present for x ≥ 0.1 at low temperatures [14]. Comparing the observed peaks with the corresponding energy IR-active phonons [13] and concerning the results from the oxygen isotopic substitution certain possibilities are revealed [15]. The band at ~150 cm⁻¹ (that shows a splitting at low temperatures and doping levels) can be related to the IR modes; the B₂u of La/Sr (following the Abma notation of the orthorhombic phase), the B₁u of Cu₂, the B₁u or the silent A₁ of the La/Sr atoms and finally the B₂u of the Oab with a mixture of Cu and La/Sr atoms. The wide band at ~280 cm⁻¹ with one or more of the four phonons; the B₁u symmetry of Oapex and Oab, the silent A₁ of the Oab atoms and the B₃u phonon of the Cu₂ or of the Cu with a mixture of La/Sr and Oab atoms. Finally the ~370 cm⁻¹ with the B₂u phonon of the Oapex. Such assignment agrees with the data obtained from a single LSCO crystal with x = 0.17 [11].

The band at ~150 cm⁻¹ usually appears as a double or triple peak [6] in agreement with its possible association with more than one IR phonons. The increment of the energy of the ~120 cm⁻¹ peak with doping and its large width denotes its correlation to the La/Sr vibrations of B₂u, B₁u or A₁ symmetry [16], which is in agreement to the results of Refs. [7,13] and to the assignment given in this work. The small isotopic shift of the narrow peak at ~150 cm⁻¹ and its unchanged energy with increasing doping indicate that this band can be associated with the mixture vibrations of the Cu and O atoms (B₁u or B₂u-symmetry). The other band at ~370 cm⁻¹ is the most narrow of the three, related to only one IR phonon and to oxygen vibrations perpendicular to the CuO₂ planes, so it shifts considerably with the isotopic substitution (Fig. 2).

The wide band at ~280 cm⁻¹ is assigned to a mixture of four IR phonons, three of which involve vibrations along the c-axis and the other 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 B₂u symmetry phonon of the mixture vibrations of Cu, La/Sr and Oab atoms along the ab-planes, which is expected to have smaller isotopic shift. Furthermore, the spectral shape of this mode is modified and its band width is reduced with the oxygen isotopic substitution (Fig. 2). This could not occur, unless it is composed of several modes, some shifting with the isotope change and others being unaffected. Besides it provides an explanation for the large band-width (~100 cm⁻¹) of this wide peak, which cannot be caused from only one phonon (the A₁g phonon at ~273 cm⁻¹ or the B₂u phonon along the ab-planes). The observation of a double peak in the B₁g Response function of the overdoped LSCO compound, by Chen et al. [11], in the energy region 210–240 cm⁻¹ for temperatures below and above Tc, which is not electronic, agrees with our statement of a multiple phonon band at ~280 cm⁻¹.

From the association of the D₂h point group 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 B₁u, B₃u, and A₁g phonons of D₂h are associated with the A₁g-symmetry modes of the C₃v, C₂v, and D₂ subgroups, respectively. The other possible subgroup C₃v allowed by the breaking of the inversion symmetry might be also realized, but the corresponding activated IR phonons that involve vibrations along the ab-plane may be very weak in the Raman spectra. We conclude that the appearance of the new modes is a direct evidence of the loss of the inversion symmetry. This mainly happens at low temperatures and for certain doping levels for which the compound is superconducting.

A reasonable question that appears is why the Raman modes are not seen in IR measurements and the leakage happens only the other way around, if we have an inversion symmetry breaking. The reason is that for the doped LSCO compounds (x = 0.12–0.15), it is very difficult to observe even the symmetry allowed IR modes in the IR spectra, since the signal is very weak for the metallic compounds [18,19] and therefore the observation of the Raman active modes in the IR spectra, activated by symmetry breaking is even more difficult.

The breaking of the inversion symmetry could be a direct effect of 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 continuously with Sr, at least up to 50% substitution. This is certainly not the case here because the intensity of the modes is gradually reduced above optimal doping (Fig. 5). Certainly, one has to take into account that with doping the samples become more metallic and screening effects prevent observation of phonon modes at high Sr concentrations. However, our data show that for the doped samples the intensity of the Raman forbidden modes increases at low temperatures (Fig. 4), where resistivity of the samples is decreased [20] and therefore the screening is expected to increase, contrary to the observed strengthening of the new modes. Another question concerns the close connection of the three new bands with the orthorhombic phase. Our data show that these modes appear in the Raman spectra of the doped samples obtained above and below the structural transition temperature [6]. As it is clear in Figs. 1 and 5, the band at ~370 cm⁻¹ gradually looses strength towards the orthorhombic to tetragonal phase transition.

Fig. 5. Temperature and doping dependence of the absolute intensities of the bands at ~150 cm⁻¹ and ~370 cm⁻¹. Whenever was necessary the sum of the integegraded intensities of the two or three peaks is plotted for the ~150 cm⁻¹ band.
However, the bands at ~150 and 370 cm\(^{-1}\) are clearly present even in the tetragonal phase (Fig. 2a).

In the case of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) (YBCO), in the \((xx)\) or \((yy)\) polarization, it has been reported that two phonons of corresponding energy are due to Ba (~120 cm\(^{-1}\)) and Cu (~150 cm\(^{-1}\)) phonons with vibrations along the c-axis. These two low energy phonons show a gradual modification in intensity with doping [21]. Besides, the width of the Ba phonon is considerably increased away from stoichiometry, while the width of the Cu atoms remains small at all doping levels [21]. In YBCO the disorder is introduced at levels lower than optimal doping from vacancies in the chains and affects the Ba phonon, from the charge transfer that takes place via the apical oxygen of the BaO planes. In the case of LSCO however Sr substitution for La is probably a source of disorder but at the same time it provides the carriers to the CuO\(_2\) planes. This discriminates the two cuprate families, since in YBCO optimal doping signifies a less disordered lattice, while in LSCO the disorder should increase continuously, even beyond optimal doping.

Although it was not possible to follow the temperature for the appearance of two from the three new bands (150 cm\(^{-1}\) and 370 cm\(^{-1}\)), which for certain doping levels is present even at room temperature, we have seen at RT that their doping dependence follows the \(T_c\) dependence on \(x\) [6]. Besides, we can have an estimate of the doping dependence of this temperature (\(T'\)) that the wide band at 280 cm\(^{-1}\) disappears. The \(T'\) value was estimated as the temperature at which the intensity of this mode was roughly 20% of the strongest one, so as to be sure that what we observe is the 280 cm\(^{-1}\) band and not only a fluctuation in the background and is presented in Fig. 6 in connection with \(T_c\). Apparently this wide band develops at temperatures well above \(T_c\) and with a doping dependence resembling closely the latter, including the plateau near \(x = 1/8\).

It appears that the symmetry breaking and the activation of several IR modes forming the bands at ~150 cm\(^{-1}\), ~280 cm\(^{-1}\), and ~370 cm\(^{-1}\) in the LSCO compounds is related with local lattice distortion. This could be induced from the Sr substitution for La. However, it is unclear what would cause the decrease in intensity of the IR modes in the overdoped region because the disorder from the substitution should continuously increase up to the highest Sr concentrations studied and screening effects cannot explain the intensity variations of these modes. Nevertheless the data indicate that it is possible for certain doping levels and at low temperatures, the apparent local lattice distortions to acquire a long range order, which diminishes in the overdoped region and high temperatures, even though the X-ray data do not indicate such ordering [22]. It maybe that the effects are dynamic in nature and as they freeze at low temperatures they establish an ordered state detectable by Raman spectroscopy. The correlation of this ordering with the \(T_c\) is an indication of its connection to superconductivity. Notably, similar behavior in doping and temperature has been reported in LSCO from magnetization experiments [23,24]. Thermal and magnetic hystereses were reported to develop within this temperature and doping region due to currents associated to superconductivity.

The reduction of the crystal symmetry will affect the symmetry and the coupling of the order parameters as well [25]. Inversion symmetry implies parity conservation and the order parameters allowed by the crystal symmetry (irreducible representations) will have a well defined parity (odd or even). The breaking of the inversion symmetry is expected to mix the two parities and the corresponding order parameters. The weak breaking of symmetry may affect \(T_c\) provided that two order parameters of appropriate symmetry can be realized. This could be another reason for the connection between \(T_c\) and the IR modes that appear in the Raman spectra (Fig. 4).

In a study of \(\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4\) with EXAFS, two Cu-O\(_2\) bond lengths for temperatures below 100 K (i.e. in the orthorhombic phase) and similar variations for the tilting angle of the octahedra have been detected. Based on those results two types of stripes have been proposed related to the normal (undistorted) and distorted octahedra being parallel to the \(a\)-axis [26]. The existence of stripes would induce a breaking of the local inversion symmetry and therefore one expects IR modes to become Raman active. The evolution of certain IR modes indicates that originally the two bond lengths are ordered randomly at least close to room temperature. With lowering temperature and for certain doping levels, an ordering of those local distortions occurs, which decreases the bandwidth of specific IR modes.

The ordering of the local distortions for certain doping levels and at low temperatures should reduce the initial symmetry to \(C_{4v}\), enhancing one \(B_{1g}\) phonon. This may correspond to stripes parallel to the \(a\)-axis suggested by Bianconi et al. [26]. The narrow subband at ~150 cm\(^{-1}\) that appears strong and weak at low temperatures (Fig. 1) should then correspond to the \(B_{1g}\) phonon of the Cu atoms, in agreement with the previous assignment of this narrow band. The long range ordering of those distorted unit cells can then form stripes, or other structures like checkerboard or more generally a nanoscale phase separation. In addition, a local dipole moment could be created from the uneven distribution of the carriers above and below the CuO\(_2\) symmetry plane behaving possibly as polarons.

Another possible origin of the breaking of the inversion symmetry may be the electric field that exists across the CuO\(_2\) planes in both YBCO and LSCO. This can originate from the uneven ion charge Ba\(^{2+}\) and \(Y^{3+}\) for YBCO or La and La/Sr for LSCO. The electric field coexists and interacts with the carriers introduced by the doping procedure causing 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 apparently preformed at temperatures well above \(T_c\) will be destroyed at high doping levels, as indicated by the disappearance of the symmetry breaking induced IR modes.

### 5. Conclusions

In this work 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. Although we cannot exclude the possibility some of these bands to be associated to peaks in the phonon density of states, the association of them with IR modes with eigenvectors not only within the ab-plane but also along the c-axis is an explanation that can match all experimental data. The temperature dependence of these modes varies with doping in a manner similar to \( T_c \). This can be attributed to the formation of dynamic local lattice distortions that break inversion symmetry. These lattice modifications are frozen at low temperature and become detectable by Raman spectroscopy.

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