Hydrostatic pressure induced lattice effects in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \)

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Abstract. Micro-Raman measurements under hydrostatic pressures up to \( \sim \)6 GPa have been carried out on high-quality \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) polycrystalline compounds with Sr concentration up to \( x=0.24 \). The \( zz \) scattering polarization has been investigated at room temperature, where two strong modes due to La/Sr and the apex oxygen atoms are observed. The energy of the strong modes increases almost linearly with pressure for the Sr concentrations studied. Modifications in the increment rate \( d\omega/dp \) have been detected depending on the amount of doping. Finally, measurements at low temperatures denote that the application of pressure minimizes the distortions of the \( \text{CuO}_6 \) octahedra.

1. Introduction

Previous Raman studies have given strong evidence of local lattice distortions in the cuprates, which are induced at room temperature by varying the hydrostatic pressure and correlate with changes in the superconducting transition temperature, \( T_c \). Anomalous nonlinear pressure dependence is observed for almost all \( A_g \) phonons of the \( \text{YBa}_2\text{Cu}_3\text{O}_6 \), \( \text{YBa}_2\text{Cu}_{2}\text{O}_{6.5} \), \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) and \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \) superconducting single crystals, which occurs at pressures where \( T_c \) shows also characteristic changes [1, 2, 3]. The results are compared with a similar correlation found between transition temperature and spectral modifications in \( \text{YBa}_2\text{Cu}_3\text{O}_x \) and \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO) by chemical doping [4, 5]. There are strong indications that the saturation of \( T_c \) with pressure or compositional doping in these cuprates is mainly related with lattice instabilities and probably also with phase separation phenomena. The above mentioned results motivated us to carry out micro-Raman measurements under hydrostatic pressures up to \( \sim \)6 GPa for the LSCO compound, which shows a variety of phases with doping and temperature [6]. As a function of increasing strontium content, there is a structural phase transition from a low temperature orthorhombic (LTO) to a high temperature tetragonal (HTT) phase. Within the orthorhombic phase there is a tilting of the \( \text{CuO}_6 \) octahedra, which vanishes by approaching the structural transition temperature, \( T_{ot} \). It is known that pressure affects strongly the structural properties of this compound (orthorhombic phase is suppressed under pressure, i.e., \( T_{ot} \) decreases with pressure) while it is not expected to affect strongly the superconducting properties, since LSCO does not have a charge reservoir layer (like the Cu-O chains in \( \text{YBa}_2\text{Cu}_3\text{CuO}_x \) [7, 8, 9, 10, 11, 12]. Yamada and Ido [12] showed that the maximum
increase of the superconducting transition temperature with pressure, \(dT_c/dp\) occurs for the \(x=0.15\) compound, and \(T_c\) increases from 38 K, at ambient pressure, to 42K at \(\sim 2\) GPa.

In this work, a micro-Raman study of high-quality LSCO polycrystalline compounds with \(x=0.06−0.24\), has been carried out in order to examine the effect of high hydrostatic pressure on the phonon modes and provide information about possible pressure induced local structural modifications. At room temperature, only the strong La/Sr and apex oxygen modes of \(A_g\) symmetry [13, 14, 15, 5], have been studied. The soft mode at \(\sim 100\) cm\(^{-1}\), which is correlated with the LTO-HTT phase transitions and appears only in the orthorhombic phase of the low Sr concentration samples has not been observed [13, 14]. Also, the symmetry forbidden bands, which are mainly observed in the low temperature \(xx/yy\) polarization spectra of the doped samples [13, 14, 15, 16], have been examined at high pressures.

The experimental details of the sample preparation and the Raman measurements are described elsewhere [5, 17].

2. Results and discussion

Figure 1 presents typical Raman spectra for selected hydrostatic pressures at room temperature for the \(x=0.24\) compound. For all compounds studied at room temperature, only the two strong phonons of the La/Sr and apex oxygen atoms of \(A_g\) symmetry are clearly observed. The energy of both these phonons increases almost linearly with pressure for all Sr contents. However, it is worth noticing that, for the La/Sr phonon, the energy increment rate \(d\omega/dp\) decreases considerably for the optimally doped and overdoped compound (see Table 1 and Fig. 2). It is known that the increment rate \(dT_c/dp\) also decreases with increasing amount of doping (see for example ref. [12]). Since the carriers in LSCO sample are introduced in CuO\(_2\) planes through the substitution of La\(^{+3}\) for Sr\(^{+3}\), the decrease of \(d\omega/dp\) for the La/Sr phonon with doping may denote a connection with the variation of \(T_c\) with pressure. Concerning the apex phonon, \(d\omega/dp\) is almost constant with doping or slightly decreases (Fig.2).

| Material   | La/Sr phonon | Apex phonon |
|------------|--------------|-------------|
| \(La_{1.94}Sr_{0.06}CuO_4\) | 3.77±0.89    | 4.82±0.96   |
|           | [1.7±0.4]    | [1.1±0.2]   |
| \(La_{1.99}Sr_{0.07}CuO_4\) | 3.52±0.98    | 4.78±0.96   |
|           | [1.6±0.4]    | [1.1±0.2]   |
| \(La_{1.85}Sr_{0.15}CuO_4\) | 2.19±0.91    | 4.01±0.99   |
|           | [1.0±0.4]    | [0.9±0.2]   |
| \(La_{1.76}Sr_{0.24}CuO_4\) | 2.75±0.97    | 4.24±0.98   |
|           | [1.3±0.4]    | [1.0±0.2]   |

Mixed polarization high pressure spectra from low temperatures measurements for the \(x=0.06\) and 0.07 samples at \(\sim 5.5\) and 2.8 GPa are presented in Figs. 3 and 4, respectively. As can be seen in these figures the soft mode in the low energy region of the spectra has not been detected. It is known that at atmospheric pressure this soft mode peak appears above 250K for these two Sr contents [5]. The disappearance of this peak suggests that the tilting angle of the
**Figure 1.** Typical room temperature Raman spectra of the La$_{1.76}$Sr$_{0.24}$CuO$_4$ compound for selected hydrostatic pressures.

**Figure 2.** The variation of the measured rate of energy increase with hydrostatic pressure of the La/Sr and apex oxygen phonons as a function of Sr content.

**Figure 3.** Typical low temperature Raman spectra from a crystallite of the La$_{1.94}$Sr$_{0.06}$CuO$_4$ sample at ~5.5 GPa.

**Figure 4.** Typical low temperature Raman spectra from a crystallite of the La$_{1.93}$Sr$_{0.07}$CuO$_4$ sample at ~2.8 GPa.
CuO$_6$ octahedra is very small (or even zero) and the orthorhombicity has been suppressed with pressure. Therefore, the $T_{\text{ot}}$ in this case must be less than 77 K for both samples studied.

At ambient pressure certain new modes appear at $\sim$150 cm$^{-1}$, $\sim$280 cm$^{-1}$, and $\sim$370 cm$^{-1}$ mainly in the superconducting doping region and at low temperatures [13, 14, 16]. These modes have been attributed to IR phonons activated in the Raman spectra from the breaking of the inversion symmetry [18]. At high hydrostatic pressures only traces of the $\sim$150 cm$^{-1}$ band can be seen at very low temperatures (Figs. 3 and 4). On the other hand, the intensity of the other IR mode at $\sim$370 cm$^{-1}$ increases considerably in the high pressure low temperature spectra and becomes even stronger than the apical oxygen (Figs. 3 and 4). Since the mode has an increased width at high pressures and it is mixed with the $\sim$280 cm$^{-1}$ broad band, no quantitative conclusions can be drawn for its pressure and temperature dependence. Since the three new bands are related with IR phonons of different symmetry, the data may indicate that the high pressure alters the local symmetry and affects the intermediate phase marked by the appearance of the IR modes, which is formed above $T_c$. It should be mentioned the considerable increase with pressure in the intensity of the $B_{3g}$ mode at $\sim$480 cm$^{-1}$ of the planar oxygen atoms. This apparently reflects a charge redistribution that occurs at high pressures and reduces the screening of certain phonons within the CuO$_2$ planes.

Concerning the apex mode, it is known that at ambient pressure its energy is practically unchanged in the temperature range 10-295K, for Sr contents up to $x=0.17$ [16]. This result has been correlated with the existence of distorted octahedra CuO$_6$. However, at high pressures, above 210-220 K, a sudden energy decrease, of about 5 cm$^{-1}$, has been observed, for the samples studied (Figs. 5 and 6). This result may denote that the application of high hydrostatic pressure minimizes such lattice distortions in the temperature range 220-295 K. Finally, the La/Sr phonon energy shows the same behavior as at room temperature, i.e., it decreases with temperature.
3. Conclusions
The energies of the La/Sr and apex oxygen phonon modes increase almost linearly with pressure, at room temperature, for all Sr concentrations studied. The decrease of $\frac{d\omega}{dp}$ for the La/Sr phonon with doping may denote a connection with the variation of $T_c$ with pressure. The low temperature spectra at high pressures indicate a modified local symmetry and probably a charge redistribution within the CuO$_2$ planes. The apex mode behavior denotes that the application of pressure minimizes the distortions of the CuO$_6$ octahedra.

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