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Doping and temperature dependence of inversion symmetry breaking in $La_{2-x}Sr_xCuO_4$

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ABSTRACT

The doping dependence of the Raman spectra of high quality $La_{2-x}Sr_xCu^{16,18}O_4$ polycrystalline compounds has been investigated at low temperatures. It is shown that symmetry forbidden bands peaked at ~150 cm^{-1}, ~280 cm^{-1}, and ~370 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 $q \cong 0$ phonons in the Brillouin zone. $La_{2-x}Sr_xCuO_4$ (LSCO) is a typical example of the cuprate family showing a variety of phases with doping and temperature [1,2]. LSCO displays a characteristic soft mode of A_g symmetry at ~100 cm^{-1} attributed to tilting vibrations of the CuO_6 octahedra about the diagonal (110) axis and activated by the High Temperature Tetragonal (HTT) to Low Temperature Orthorhombic (LTO) phase transition [3–5]. Furthermore two strong Raman active modes are attributed to the A_g vibrations of the La/Sr and apex oxygen atoms along the c-axis. Low temperature studies 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 concentration at which the compound attains the maximum superconducting transition temperature (T_c) [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 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 ~150 and ~370 cm^{-1} appeared in the xx polarization Raman spectra and at low temperatures a broad peak at ~280 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 $y(zz)\bar{y}$ and $y(xx)\bar{y}$ (or $x(yy)\bar{x}$) scattering configurations from individual microcrystallites of a series of high quality $La_{2-x}Sr_xCuO_4$

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compounds and for $x = 0.0$, 0.015, 0.125, and 0.15 with ~85% isotopic substitution of ^{18}O for ^{16}O. A Jobin–Yvon T64000 triple spectrometer equipped with a liquid nitrogen cooled CCD and a microscope (magnification 100) was used for detection. The excitation beam at 514.5 nm from an Ar^+ laser was kept at very low power level securing low heating of the compound as induced from the energy shift of the very sensitive to temperature soft mode. Low temperatures were achieved using an open cycle Oxford CF1104 cryostat operating with liquid nitrogen and liquid helium.

3. Results

Raman spectra for selected temperatures for the $La_{2-x}Sr_xCu^{16}O_4$ 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 ~229 cm^{-1} and of the apical oxygen at ~ 429 cm^{-1}, three, non predicted from symmetry, 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. 1). In the other scattering polarization (*zz*), the soft mode and two weak narrow peaks (the other three A_g-symmetry phonons) at ~156 cm^{-1} and ~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 ~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_1-symmetry and as a result the three new bands cannot 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.

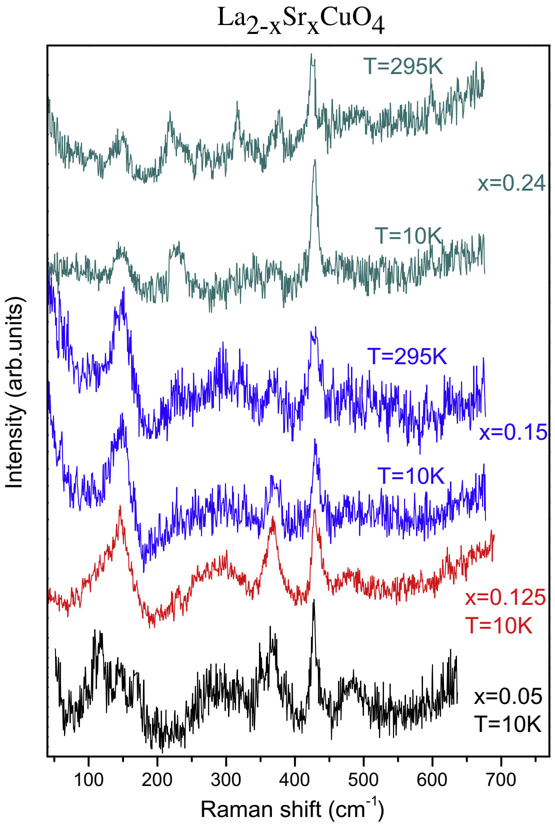

Fig. 1. Typical Raman spectra for selected temperatures for the $La_{2-x}Sr_xCu^{16}O_4$ compound with $x = 0.05$–0.24 in the $x(yy)\bar{x}$ scattering geometry, using the 514.5 nm excitation wavelength.

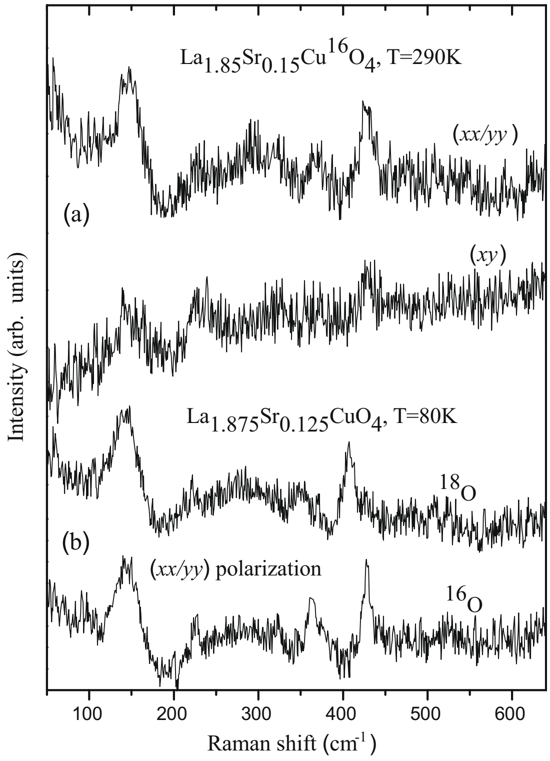

Fig. 2. Raman spectra for the $La_{1.85}Sr_{0.15}Cu^{16}O_4$ in the parallel and crossed polarizations (a) and for $La_{1.875}Sr_{0.125}CuO_4$ for parallel polarizations and two oxygen isotopes (b).

At low temperatures the band at ~150 cm^{-1} undergoes a spectral modification and appears as a double peak, a wide one at ~120 cm^{-1}, a narrower one at ~150 cm^{-1} and at low Sr doping levels ($x \leqslant 0.07$) as a triple peak with the additional contribution of a weak peak at ~170 cm^{-1} (Fig. 3) [6]. The deconvolution of the low energy region into subbands, indicates that the narrow peak at ~150 cm^{-1} remains constant in energy independent of doping, while the wide component at ~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 ~120 cm^{-1} diminishes around $x \approx 0.20$ and for higher Sr concentrations only the narrow peak at ~150 cm^{-1} has been detected.

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

Similar bands at ~150 cm^{-1}, ~280 cm^{-1}, and ~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