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Anharmonicity and Weak Mode Assignment in $La_{2-x}Sr_xCuO_4$ with Oxygen Isotopic Substitution

E. Siranidi[a,*], D. Lampakis[a], D. Palles[a], E. Liarokapis[a]
and K. Conder[b]

[a]Department of Physics, National Technical University, Athens 157 80, Greece
[b]Paul Scherrer Institut (PSI) WLGA, Villigen PSI 5232, Switzerland

The oxygen isotope effect on the first- and second-order Raman active modes of high-quality $La_{2-x}Sr_xCu^{16,18}O_4$ (80% substitution ^{16}O by ^{18}O) polycrystalline compounds with $x = 0.00$, 0.015 was investigated at low temperatures. In the second-order Raman scattering several weak and strong peaks were observed and assigned to oxygen atom vibrations. With the isotopic substitution the apex oxygen mode follows quite well the mass harmonic law at all temperatures studied, while the soft mode is anharmonic in the temperature range of 77–180 K and for higher temperatures its anharmonicity is strongly increased. The temperature dependence of the energy of the soft mode for $x = 0.0$ shows also a modification at ≈ 180 K and an abnormal behaviour at ≈ 280 K, which may be related with the transition to the antiferromagnetic phase.

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1. Introduction

The system $La_{2-x}Sr_xCuO_4$ is derived from the parent compound La_2CuO_4, which is an insulating antiferromagnet and shows a variety of phases including superconductivity upon doping. The substitution of La^{3+} by the slightly larger Sr^{2+} reduces the orthorhombic distortion and the structural transition temperature [1]. The substitution of ^{16}O by the heavier ^{18}O is expected to decrease the energy of the oxygen phonons due to the mass difference and provide some insight on the possible anharmonic effects in this compound. In the following, the oxygen isotope effect will be examined in order to identify those modes (first and second order) mainly related with vibrations of the oxygen atoms. The behaviour of the soft mode at low temperatures is investigated in detail as expected to show a stronger anharmonicity than the normal modes.

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[*] corresponding author

2. Experiment

Polycrystalline compounds of high-quality $La_{2-x}Sr_xCu^{16,18}O_4$ (80% substitution ^{16}O by ^{18}O) with $x = 0.00$, 0.15 have been prepared by the solid state reaction technique and examined using the Raman spectroscopy. The Raman spectra were obtained at nominal temperatures of 77 K to room temperature (RT) with a T64000 Jobin-Yvon triple spectrometer equipped with a liquid nitrogen cooled charged coupled device (CCD) and a microscope (magnification ×100). The 514.5 nm line of an Ar^+ laser was used for excitation. Low temperature measurements were achieved using an Oxford micro-He 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 $y(zz)\overline{y}$ and $y(xx)\overline{y}$ (or $x(yy)\overline{x}$) scattering configurations. Appropriately very low laser power densities were necessary to avoid sample heating at the laser spot. As a result, accumulation times were of the order of 3–14 hours.

3. Results and discussion

Typical Raman spectra of $La_2Cu^{16,18}O_4$ in the approximate $y(zz)\overline{y}$ scattering configuration at nominal temperatures of 78 K and RT and of $La_{1.985}Sr_{0.015}Cu^{16,18}O_4$ at RT are presented in Fig. 1a and b, respectively. In this polarization configuration four modes are Raman active and it is easily observed that three of them are shifted due to the oxygen isotopic substitution and therefore mostly involve vibrations of the oxygen atoms. Only the phonon at ≈ 227 cm^{-1} which is not shifted with the substitution of ^{16}O by ^{18}O has been attributed to the vibrations of the La (or La/Sr in $La_{2-x}Sr_xCuO_4$) atoms [2, 3].

The relative shift of the soft mode and the apex oxygen mode of $La_2Cu^{16,18}O_4$ as a result of the oxygen isotope effect is presented in Fig. 2a. The soft mode shows a deviation from the harmonic law at all temperatures studied. At low temperatures ($T < 180$ K) the relative shift is $\approx 4\%$ which is lower than the nominal one ($\approx 5\%$). Approaching the room temperature the deviation from the harmonic law becomes more intense, as the relative shift gradually decreases to $\approx 2.3\%$. On the contrary, the apex oxygen mode follows quite well the mass harmonic law, at all temperatures studied.

Figure 2b shows the temperature dependence of the energy of the soft mode in $La_2Cu^{16,18}O_4$. As expected, the energy decreases with increasing temperature but it appears that at $T \approx 280$ K approaches a local minimum and then it increases again towards the room temperature for both oxygen isotopes. The energies were determined by fitting the spectra with Lorentzian curves and the error of the fitting is estimated to be smaller than 0.4 cm^{-1}. In order to investigate the effect of the laser induced local heating, we have studied in detail the dependence of the Raman spectra on the laser power density. Based on those measurements we have chosen the lowest possible laser intensity that will secure a low shift of the soft mode from the heating and at the same time allow the experimental studies in an appropriate

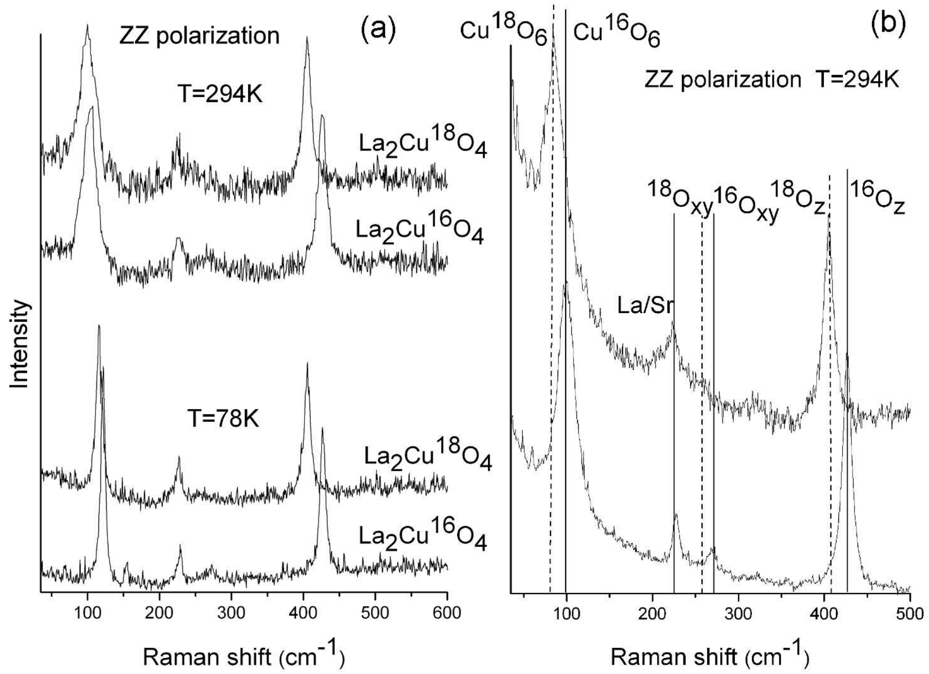

Fig. 1. Typical Raman spectra in the approximate zz polarization of (a) $La_2Cu^{16,18}O_4$ and (b) $La_{1.985}Sr_{0.015}Cu^{16,18}O_4$.

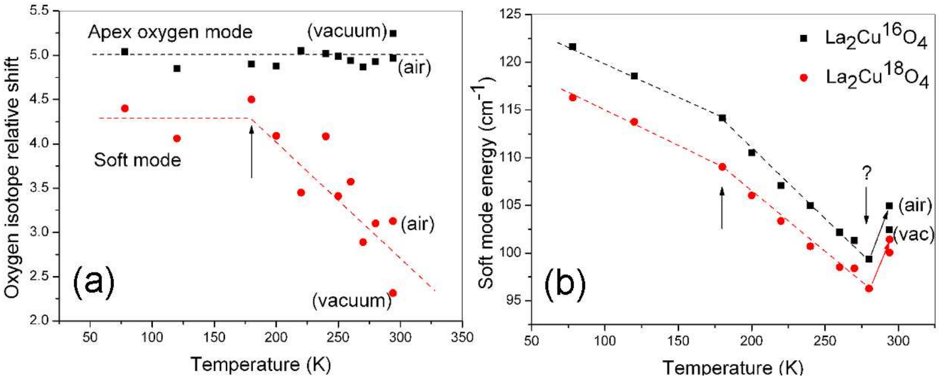

Fig. 2. (a) The relative shift of the soft mode and the apex oxygen mode due to the oxygen isotopic substitution in $La_2Cu^{16,18}O_4$. (b) Temperature dependence of the soft mode energy in $La_2Cu^{16,18}O_4$.

time. In this way the shift from the heating, as estimated from the comparison of the soft mode energy at RT in vacuum and in air (Fig. 2a and b), was ≈ 2 cm^{-1} for $La_2Cu^{16}O_4$ and ≈ 1 cm^{-1} for $La_2Cu^{18}O_4$, which is expected to be the same in the temperature interval under investigation. Therefore, the detected abnormal behavior close to RT cannot be due to any local crystal heating of the sample. The temperature dependence in the pure La_2CuO_4 compound shows also a clear modification at ≈ 180 K (Fig. 2b), which correlates with the onset temperature to higher anharmonicity in Fig. 2a. At this point it is not clear what is the origin of the two effects, but the compound undergoes a phase transition to an antiferromagnet approximately at room temperature and the results may indicate a coupling of the magnetic ordering with the lattice.

Typical Raman spectra of $La_2Cu^{16,18}O_4$ in the first and second order xx polarization at nominal temperatures of 78 K and RT and of $La_{1.985}Sr_{0.015}Cu^{16,18}O_4$ in the first order xx polarization at RT are presented in Fig. 3a and b, respectively. In the xx polarization several strong and weak modes have been observed. The energies of these peaks are in agreement with the ones observed in previous reports [2–4].

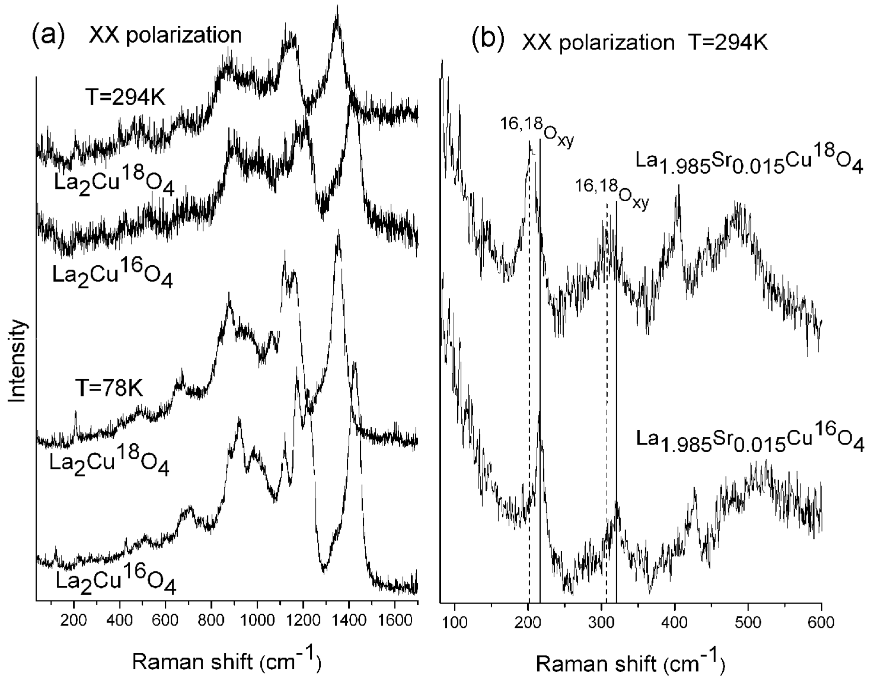

Fig. 3. Typical Raman spectra in the approximate xx polarization of (a) $La_2Cu^{16,18}O_4$ and (b) $La_{1.985}Sr_{0.015}Cu^{16,18}O_4$.

All peaks observed in the zz polarization were present also in the xx spectra, except for the La/Sr mode at ≈ 227 cm^{-1}, which disappears in the xx scattering configuration. Two modes at ≈ 220 cm^{-1} and ≈ 320 cm^{-1} in the first order spectra that appear only in the xx spectra, are shifted due to the oxygen isotopic substitution and therefore involve vibrations of the oxygen atoms [5]. This is in agreement with Weber et al. [3], who suggested that these modes are due to oxygen vibrations in the xy planes.

All modes in the second order Raman spectra are shifted due to the substitution of ^{16}O by ^{18}O and therefore are attributed to the vibrations of the oxygen atoms. Furthermore, the intensities of the two phonon peaks decrease with increasing temperature, in agreement with Sugai [2].

4. Conclusions

Concluding, we examine the oxygen isotope effect on polycrystalline $La_{2-x}Sr_xCuO_4$ ($x = 0.00$, 0.015) compounds via micro-Raman measurements. We remark the anharmonicity of the soft mode, which increases substantially for temperatures above ≈ 180 K becoming at RT half of the nominal one. We also systematically examined the temperature dependence of the energy of this mode and observe anomalous behavior at ≈ 180 K and close to RT. The latter is reminiscent of the phase transition temperature to the antiferromagnetic ordering probably indicating a coupling of the magnetic ordering with the lattice. Finally, we investigate the first and second order Raman xx spectra at low temperatures and confirm that all the two-phonon peaks at 800–1500 cm^{-1} are attributed to the vibrations of the oxygen atoms.

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References

[1] B. Keimer, N. Belk, R.J. Birgeneau, A. Cassanho, C.Y. Chen, M. Greven, M.A. Kastner, A. Aharony, Y. Endoh, R.W. Erwin, G. Shirane, *Phys. Rev. B* **46**, 14034 (1992).

[2] S. Sugai, *Phys. Rev. B* **39**, 4306 (1989).

[3] W.M. Weber, C.R. Peters, E.M. Logothetis, *J. Opt. Soc. Am.* **6**, 455 (1989).

[4] W.M. Weber, C.R. Peters, B.M. Wanklyn, C. Chen, B.E. Watts, *Phys. Rev. B* **38**, 917 (1988).

[5] D. Lampakis, Ph.D. Thesis, National Technical University of Athens, Department of Physics, Athens 2002, p. 100.