

Thermally activated dynamics of the tilts of the CuO_6 octahedra, hopping of interstitial O, and possible instability towards the LTT phase in $\text{La}_2\text{CuO}_{4+\delta}$

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The anelastic spectrum (dynamic Young's modulus and elastic energy absorption) of $\text{La}_2\text{CuO}_{4+\delta}$ has been measured between 1 and 700 K with $0 < \delta < 0.02$. The spectrum of stoichiometric La_2CuO_4 in the low-temperature orthorhombic (LTO) phase is dominated by two intense relaxation processes which cause softening of 16% around 150 K and 9% below 30 K at $f \sim 1$ kHz. The relaxation at 150 K is attributed to the presence of a fraction of the CuO_6 octahedra which are able to change their tilted configuration by thermal activation between orientations which are nearly energetically equivalent, possibly within the twin boundaries. The relaxation below 30 K is governed by tunneling, and involves a considerable fraction of the lattice atoms. It is proposed that the double-well potentials for the low-temperature relaxation are created by the tendency of the LTO phase to form low-temperature tetragonal (LTT) domains, which however are not stabilized like when La is partially substituted with Ba. On doping with excess O, the relaxation rates of these processes are initially enhanced by hole doping, while their intensities are depressed by lattice disorder; an explanation of this behavior is provided. Excess O also causes two additional relaxation processes. The one appearing at lower values of δ is attributed to the hopping of single interstitial O^{2-} ions, with a hopping rate equal to $\tau^{-1} = 2 \times 10^{-14} \exp(-5600/T)$ s. The second process is slower and can be due to O pairs or other complexes containing excess O. [S0163-1829(98)03210-X]

I. INTRODUCTION

The oxides of the $\text{La}_{2-x}\text{M}_x\text{CuO}_{4+\delta}$ series ($M = \text{Sr}, \text{Ba}$) display a complex structural and magnetic phase diagram, and several interconnected phenomena, like lattice instabilities and modulations, charge modulation and segregation, and suppression of the superconductivity at certain values of doping.

The structural phases of $\text{La}_{2-x}\text{M}_x\text{CuO}_{4+\delta}$ can be described in terms of tilts of the CuO_6 octahedra which compose the lattice around axes which lay in the CuO_2 planes;^{1,2} since the CuO_6 octahedra are relatively rigid and hinged to each other at their corners, the tilt of one of them propagates to the surrounding ones, resulting in a long-range-ordered pattern of tilts. It is usual to express the rotations in terms of the angles Q_1 and Q_2 around the $[110]$ and $[1\bar{1}0]$ axes (the $[100]$ direction in the tetragonal structure is parallel to the in-plane Cu-O bonds). The possible phases are the high-temperature tetragonal (HTT) with $Q_1 = Q_2 = 0$, the low-temperature orthorhombic (LTO) with $|Q_1| \neq |Q_2| = 0$ or $|Q_2| \neq |Q_1| = 0$, the low-temperature tetragonal (LTT) with $|Q_1| = |Q_2| \neq 0$, equivalent to a rotation about the $[100]$ axis,

and a phase intermediate between the LTO and LTT, generally indexed as $Pccn$, with $|Q_1| \neq |Q_2| \neq 0$. The HTT phase transforms into the LTO at a temperature T_{d1} , which is 530 K for stoichiometric La_2CuO_4 but strongly decreases on doping by substituting La^{3+} with M^{2+} (Refs. 1,3) or introducing interstitial O.⁴ It should be noted that in the new phase the octahedra are also distorted.^{5,6} The LTO phase tends to transform into LTT or $Pccn$ at a lower temperature T_{d2} in $\text{La}_{2-x}\text{M}_x\text{CuO}_{4+\delta}$ ($M = \text{Ba}, \text{Sr}$), but the formation of stable LTT domains seems to require a mismatch between the ionic radii in the La sublattice. In fact, when La is partially substituted with the much larger Ba ion, the LTT phase is stable below $T_{d2} < 70$ K; instead with Sr, having an intermediate size, the formation of LTT domains in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ can only be stimulated by the simultaneous partial substitution of La with a smaller ion, like Nd.^{2,7} This is explained by supposing that the distortion of the four octahedra around a pair of Sr^{2+} and Nd^{3+} ions (along c) induces a tilt pattern which is equivalent to the superposition of LTT and LTO domains.⁷ There is also a strong interplay between the rotations and distortions of the CuO_6 octahedra

and the electronic properties. Static magnetic and charge modulations have been observed by neutron diffraction to appear in the LTT phase,^{8,9} favored by the lattice potential of that structure; conversely, it has been proposed that the LTT phase is stabilized around $x=1/8$ by a spin- or charge-density wave commensurate with the lattice and due to charge transfer between the in-plane O atoms which are made inequivalent by the new tilt pattern^{2,10} (in the LTO phase all the in-plane oxygens are either above or below the plane, while in the LTT phase there are also the O atoms laying on the rotation axes exactly within the plane). The charge-density wave is thought to be the cause of the suppression of superconductivity in a narrow range around $x=1/8$.^{2,7-9,11} The LTT phase is also characterized by structural disorder, and seems to be always accompanied by the intermediate *Pccn* one.^{11,10} Both types of tilts have also been observed in the twin boundary regions of LTO $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (Ref. 3), and it is under debate whether the formation of the LTT phase occurs through a widening of the domain walls¹² or is mainly nucleated within the LTO domains.¹³

Signs of the tendency of the LTO lattice to form LTT domains also in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and even in La_2CuO_4 are the large anisotropic vibration amplitudes of the O atoms deduced by neutron diffraction,⁶ the low energies of the phonon modes involved in the rotations of the octahedra¹⁴ and a softening of the in-plane shear below 50 K in $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$.¹⁵ In addition, there are indications^{6,16-19} that the octahedra can tilt in a variety of patterns which are different from the average structure observed by diffraction experiments; in particular, the tilts of the octahedra have been observed to persist in the HTT phase,^{16,19} presumably with very low correlation lengths. Indeed, the instability of the MO_6 octahedra against tilting and their tendency to dynamically distort, also forming so-called Jahn-Teller polarons, are features common to several perovskites, including manganites²⁰⁻²² and the superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (Ref. 23).

In addition, indications exist of interplay between the ordering of interstitial O and the tilt angles.²⁴ In fact, the interstitial O atoms are mobile down to 150 K (Refs. 4,25) and separate into O-rich and O-poor phases; superstructures have also been observed in the O-rich phase due to the segregation of the interstitial atoms in occupied layers spaced by n empty layers (staging),^{26,27} and the relationship between the oxygen phase separation and the hole phase separation has to be clarified.²⁸ It appears that the modulations of the octahedral tilts, the ordering and aggregation of interstitial O, the electronic and magnetic phase separations and the superconducting properties are all interconnected to each other.

In spite of the intense experimental activity on these subjects, no indication exists on the dynamics of the octahedral tilts. Regarding the O mobility, the estimates are of indirect type,²⁵ with the exception of preliminary NQR results.²⁹ All these phenomena are coupled to strain, and therefore their dynamical aspects can be studied by acoustic techniques. In fact, the elastic energy absorption and elastic constants, i.e., the imaginary and real part of the strain susceptibilities, are directly connected with the dynamic response of the system, and provide information on phase transformations and relaxation processes. The acoustic investigations on 214 oxides

(for a review see Ref. 30) have been so far concerned with the influence of the phase transformations on the elastic moduli;^{5,15,30-35} only a few deal with the elastic energy dissipation^{31,32,36} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$, and none with that of $\text{La}_2\text{CuO}_{4+\delta}$. The main feature from ultrasonic and lower frequency measurements is a huge softening of c_{66} connected with the HTT to LTO transformation,^{5,15,31-33} accompanied by high values of the acoustic absorption from the movement of the twin walls.³² The occurrence of the LTO-LTT transformation has been seen as a much smaller effect both in the sound velocity and absorption of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at $T_{d2}=50-65$ K,³⁴ and as a dip in c_{66} in $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ (Ref. 35), but it has been suggested also for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x\sim 0.1$, where similar features were found around 10 K in the superconducting state.³⁴

We present the anelastic spectra of $\text{La}_2\text{CuO}_{4+\delta}$ with $0<\delta<0.02$ between 1 and 700 K, with four main thermally activated relaxation processes not reported before. Two of them are due to the hopping of excess O in the form of single interstitial ions and pairs or clusters. When the material is outgassed from excess O, the elastic susceptibility of La_2CuO_4 is not as flat as expected from a stoichiometric and defect-free crystal, but is dominated by an intense relaxation process with an activation energy of 0.23 eV, which we identify as thermally activated flipping of a fraction of the CuO_6 octahedra between nearly equivalent configurations, presumably within the twin boundaries. In addition, below 30 K still another intense relaxation process occurs, which we attribute to tunneling of lattice O atoms between metastable positions, possibly resulting from the tendency of the LTO lattice to form LTT domains. The dependence of these relaxation processes on doping and lattice disorder is also discussed.

II. EXPERIMENT

The samples of La_2CuO_4 and Nd_2CuO_4 were prepared from powders first treated for 18 h in air at 1050°C (90 h for Nd_2CuO_4 , in order to have a single phase), checked by x-ray diffraction, pressed and finally sintered for 18 h in air at 1050°C. The ingots were cut as bars approximately $40\times 4\times 0.4$ mm³. In order to measure the real and imaginary parts of the dynamic Young's modulus, they were suspended with thin thermocouple wires and electrostatically excited on their flexural modes; the vibration amplitude was detected by a frequency modulation technique. Since the resonant frequencies f of the flexural modes are proportional to the square root of the Young's modulus Y , the dispersion of the real part of the elastic susceptibility was obtained from $dY/Y=(f^2-f_0^2)/f_0^2$, where f_0 is a reference frequency. The imaginary part is equal to the elastic energy-loss coefficient, Q^{-1} , (reciprocal of the mechanical Q of the sample) and was measured from the width of the sample resonance or from the rate of the free decay of the vibration. All the measurements were made on cooling at rates below 0.7 K/min.

The contribution of a relaxation process to the dynamic elastic modulus, the Young's modulus Y in the present case, is³⁷

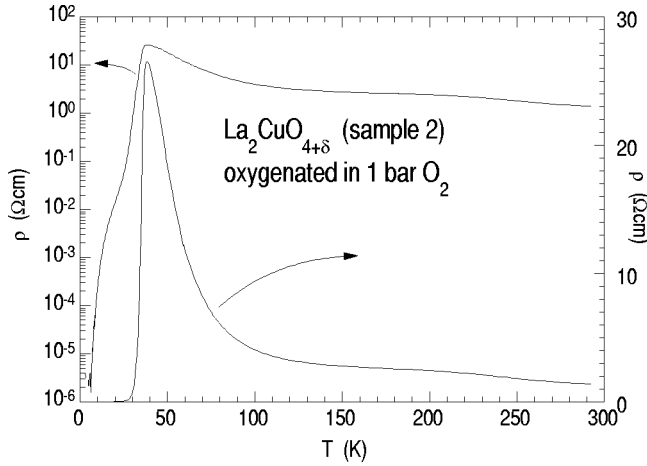


FIG. 1. Resistivity of sample 2 of $\text{La}_2\text{CuO}_{4+\delta}$ after oxygenation in 1.1 bar O_2 at 600 °C and slow cooling.

$$\left[\frac{Q^{-1}}{\delta Y/Y} \right] = \left[\frac{\text{Im}}{\text{Re}} \right] \left(\frac{\delta Y}{Y} \right) = Y v_0 c (\lambda_1 - \lambda_2)^2 \frac{f_1 f_2}{T} \frac{1}{1 + (\omega \tau)^{2\alpha}} \times \begin{bmatrix} (\omega \tau)^\alpha \\ -1 \end{bmatrix} \quad (1)$$

the imaginary part contributes to the elastic energy-loss coefficient of the sample, while the real part contributes to the dispersion of the modulus; c is the molar concentration of the defects, f_1 and f_2 are the equilibrium fractions in the two configurations 1 and 2 between which relaxation occurs with a characteristic time $\tau(T)$ which generally follows an Arrhenius law, $\tau = \tau_0 \exp(E/kT)$; λ_i is the elastic dipole of the defect in state i , i.e., the average macroscopic strain which the sample would have if each cell contained one defect in state i ; v_0 is the cell volume. The contribution of a relaxation process to the absorption is peaked at the temperature at which $\omega\tau = 1$; since τ is a decreasing function of temperature, the peak shifts to higher temperature if measured at higher ω . At the same temperature, the modulus presents a negative step with an amplitude which is twice the peak height. The Fuoss-Kirkwood width parameter α is equal to unity for pure Debye relaxation, while it broadens the peak when it is less than unity.

The crystallinity of the samples and the absence of relevant quantities of spurious phases at the grain boundaries were checked by powder x-ray-diffraction spectra taken on some of the samples in the as prepared state. In addition, the resistivity of sample 2 of $\text{La}_2\text{CuO}_{4+\delta}$ after oxygenation in 1 bar O_2 was measured. The $\rho(T)$ curve (Fig. 1) was closely comparable with those reported, for example, in Ref. 4. The superconducting transition was centered at 34 K and the resistivity below 5 K was lower than 1 $\mu\Omega$ cm, indicating a good connectivity between the grains.

The O stoichiometry of $\text{La}_2\text{CuO}_{4+\delta}$ was varied by two methods: progressive outgassing in vacuum (sample 3) and thermal treatments in static O_2 atmosphere in a quartz tube with a volume of 2 liters connected with a UHV system (sample 2). In the second case, each oxygenation was preceded by an outgassing at 700–750 °C, following the O evolution with a residual gas analyzer, in order to obtain an

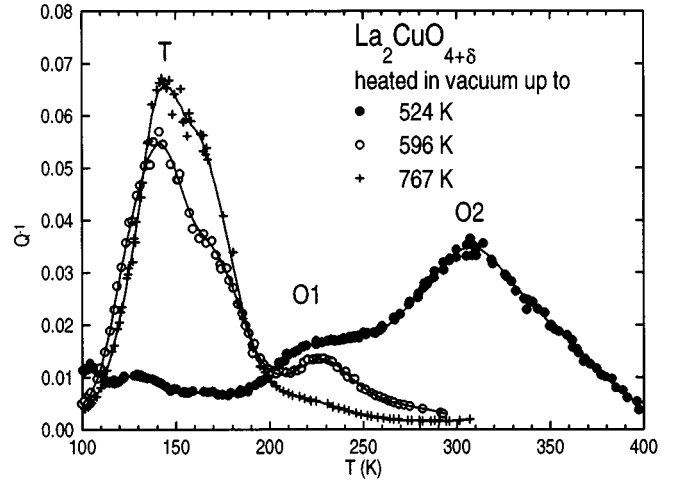


FIG. 2. Elastic energy loss of sample 3 after outgassing it in vacuum up to 524 K (closed circles, 280 Hz), 596 K (open circles, 270 Hz), and 767 K (crosses, 250 Hz).

initial reference state. The sample was then equilibrated at 620 °C for 90–120 min with a static atmosphere of pure O_2 and rapidly cooled. The initial pressures of the treatments reported here were 0.4, 0.7, 1, 10, and 835 torr O_2 ; in order to maximize the O uptake at the highest O stoichiometry, after equilibration at 820–835 torr, the sample was cooled slowly at -0.2 °C/min. In this condition the O stoichiometry was estimated to be $\delta \sim 0.018$ from the temperature of the HTT-LTO transformation (see below).

We mention that the values of δ estimated from the amount of gas absorbed were several atomic percent, i.e., higher than the values generally accepted for oxygenation at these pressures. Discrepancies are often reported in the literature between the values of δ deduced from the amount of gas absorbed and those deduced from the amount of holes doped in the CuO_2 planes (or from the mean valence of Cu), under the hypothesis that each O dopes two holes. The reason for that may be the formation of O complexes which are partially covalently bonded, and therefore introduce less than two holes per O atom.^{24,38}

It was also verified that the vacuum treatments did not cause any deterioration of the sample, by reproducing the same anelastic relaxation spectrum of sample 2 at the maximum O stoichiometry after nine outgassing and oxygenation cycles.

III. RESULTS AND DISCUSSION

A. Interstitial oxygen

Figure 2 shows the elastic energy loss of sample 3 between 100 and 400 K, after three outgassing treatments in vacuum up to progressively higher temperatures, as indicated in the figure. Three main maxima appear at 150, 230, and 305 K, labeled as T, O1, and O2, respectively. All of them shift to higher temperature at the higher vibration frequencies, denoting that they are due to thermally activated processes; this is shown in Fig. 3 for the case of intermediate δ . Peak T, which actually consists of two components, is fully developed when the sample is completely outgassed from excess O. The introduction of interstitial O depresses

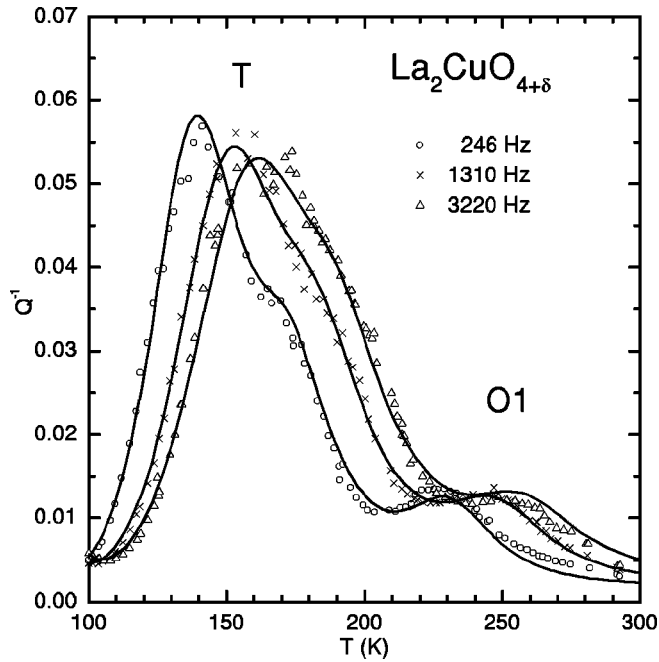


FIG. 3. Elastic energy loss of sample 3 after outgassing in vacuum up to 596 K, measured exciting three flexural vibration modes. The continuous lines are fits with broadened Debye peaks, Eq. (1) (with the same set of parameters for the three frequencies); the values of the parameters are reported in the text.

peak T, and causes the rise first of O1 and then of O2, which finally becomes predominant.

The same phenomenology is observed in sample 2 (Fig. 4), whose stoichiometry was varied by equilibration with different amounts of O_2 , as explained above. The $Q^{-1}(T)$ curves of sample 2 in Fig. 4 extend the observations to higher values of δ , at which peak O2 reaches a very high

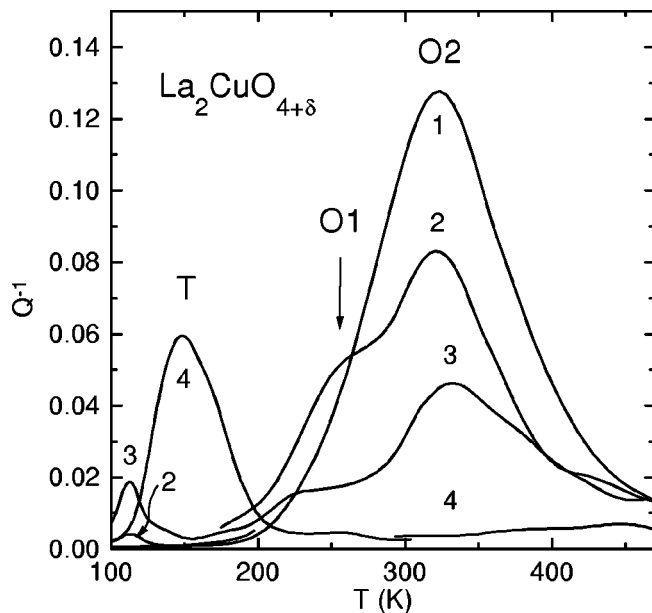


FIG. 4. Elastic energy loss of sample 2 measured at the lower vibration frequency (730–920 Hz). Curves 1–4 are obtained after equilibrating the sample at 890 K with progressively lower amounts of O_2 , as explained in the text.

intensity. The small peak at 112 K visible at intermediate O concentrations is distinct from peak T, since its temperature is lower and does not increase with the O concentration. This peak is also present in sample 3, but at lower temperature because of the lower frequency.

The two processes O1 and O2 are evidently due to interstitial O. Since O1 develops at lower values of δ , it must be due to the hopping of single interstitial atoms. It should be noted that the interstitial sites for O described in Refs. 39 and 40 would all be equivalent in a perfectly tetragonal lattice with untilted octahedra; therefore, the hopping of single O atoms among these sites would not change the local distortion and would not cause any anelastic effect [$\lambda_1 = \lambda_2$ in Eq. (1) below]. However, since the actual lattice configuration is not tetragonal, some variation of the local elastic distortion is expected when O jumps between neighboring sites. The solid lines in Fig. 3 are a fit with three peaks of the anelastic relaxation spectrum of sample 3 at intermediate concentration, measured at the three vibration frequencies; each component is the imaginary part of the contribution of a relaxation process to the dynamic elastic modulus [Eq. (1)].

The parameters describing peak O1 in Fig. 3 are $\tau_0 = (2 \pm 0.5) \times 10^{-14}$ s, $E/k = (5600 \pm 120)$ K, $\alpha = 0.7$; these values support the hypothesis of O hopping. The value of τ_0 is typical of atomic hopping with an attempt frequency close to that of the local phonon mode. Furthermore, the hopping rate τ^{-1} we estimate is in excellent agreement with the observation that the mobility of the excess O is frozen below 140–150 K;²⁵ in fact, this is the temperature range in which the mean time τ between subsequent jumps passes from 5 min to more than 1 h.⁴¹ The activation enthalpy of O1 is also close to that reported for a relaxation process previously observed by NMR and attributed to O diffusion.²⁹ On the other hand, the width of the peak is considerably higher than expected from the hopping of an isolated interstitial atom in a regular lattice, and can be explained by the variety of the arrangements of the octahedral CuO_6 units, which would give rise to a distribution of local strains. The rearrangements of the lattice structural units may also mediate the interaction between different interstitials; an indication of a correlated dynamics of the O interstitials comes from the broadening of peak O1 at increasing O concentrations, and from its shift to higher temperature, which means a slowing of the relaxation dynamics.

Peak O2 is also certainly connected with excess O, both because of its dependence on δ , and because the enormous intensity it can reach is more easily explained by hopping of atoms rather than small atomic rearrangements or polaronic distortions (which generally have smaller $\Delta\lambda$). The most simple mechanism that can be proposed for O2 is the formation of relatively stable pairs of interstitial O atoms, whose local distortion is more anisotropic than that due to the two isolated atoms, and therefore whose reorientation produces intense anelastic relaxation. The reorientation of the pair would require its dissociation and therefore would be slower than the hopping of single interstitials, so justifying the higher temperature of O2 with respect to O1. Such pairs could also be identified with the interstitial O atoms with partially covalent bond, which have been invoked to explain a doping efficiency of less than two holes per excess O atom.^{24,38}

In the doped samples we did not observe any clear sign of phase separation into O-rich and O-poor phases, nor of

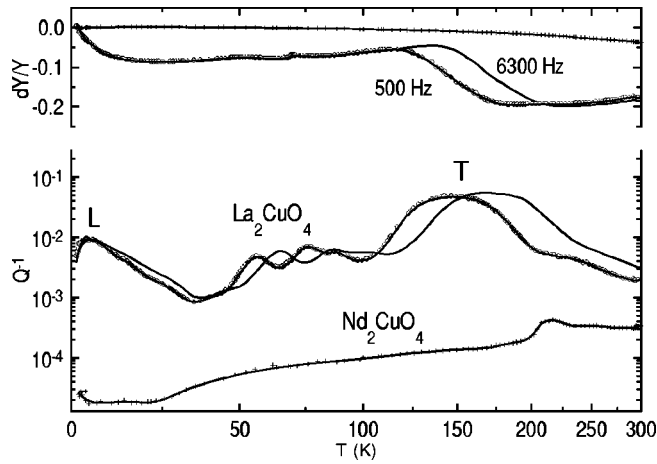


FIG. 5. Elastic energy-loss coefficient, Q^{-1} , and relative change of the Young's modulus of La_2CuO_4 (sample 1, 500 Hz and 6.2 kHz) and Nd_2CuO_4 (840 Hz).

staging^{26,27} within the O-rich phase, but it is possible that these transitions occurred and were masked by the intense relaxations O1 and O2.

B. Stoichiometric La_2CuO_4 and comparison with Nd_2CuO_4

Excess oxygen is the main defect of La_2CuO_4 and after its removal one expects a flattening of the elastic susceptibility below room temperature; on the contrary, we observe the appearance of the intense relaxation process T and the enhancement of another process below 40 K. Figure 5 compares the elastic susceptibility of stoichiometric La_2CuO_4 (after O outgassing in vacuum at 750 °C for 75 min) with that of Nd_2CuO_4 (also after annealing in vacuum up to 600 °C, which did not change much the anelastic spectrum compared to the as prepared condition). Both samples were prepared under similar conditions, with comparable dimensions and grain sizes, but the elastic susceptibility of Nd_2CuO_4 is practically flat at all temperatures, in sharp contrast with that of La_2CuO_4 . This fact evidently reflects the differences between the two structures: in Nd_2CuO_4 the O atoms are all stacked along the same lines in the c direction (T' phase),⁴² so that there are no apical oxygens and CuO_6 octahedral units, but only flat CuO_2 planes. The featureless elastic susceptibility of Nd_2CuO_4 reflects the absence of any off-center atomic position, lattice instability, or structural phase transformation,⁴³ while the changes in the slope of the $Q^{-1}(T)$ (and in the modulus at 20 K, not visible in the scale of Fig. 5) presumably reflect the changes in magnetic ordering observed at 250, 30, and 20 K by neutron-scattering experiments.⁴³ The flat anelastic spectrum of Nd_2CuO_4 confirms the reliability of the measurements and the good quality of the samples, in particular the absence of contributions from spurious phases at the grain boundaries.

The anelastic spectrum of stoichiometric La_2CuO_4 is dominated by two processes, labeled as T around 150 K and L below 30 K. We will not consider here the minor peaks between 50 and 100 K. Acoustic losses at liquid-helium temperature are generally observed in amorphous materials containing atomic tunnel systems⁴⁴ and even in polycrystalline metals which are not thoroughly purified and annealed.⁴⁵ Such losses however never exceed $Q^{-1} \leq 10^{-3}$, even in fully

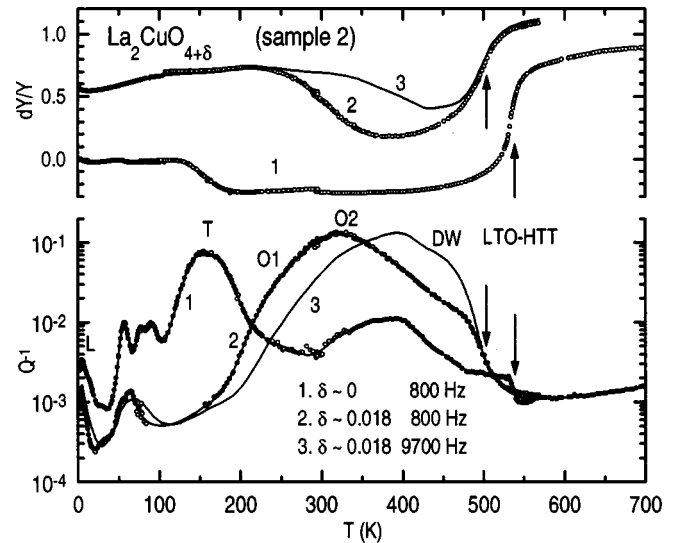


FIG. 6. Complete elastic susceptibilities of undoped and O-doped ($\delta \sim 0.018$) $\text{La}_2\text{CuO}_{4+\delta}$. The temperatures of the HTT-LTO transformations and the main relaxation processes are indicated.

amorphous samples, and therefore we exclude that peak L, whose intensity reaches $Q^{-1} \sim 10^{-2}$, is due to tunnel systems in spurious amorphous phases.

All the features of the susceptibility curves of La_2CuO_4 in Fig. 5 are shifted to higher temperature at the higher vibration frequency, indicating that they are all due to anelastic relaxation processes describable by Eq. (1), although the temperature shift of L is much less pronounced, as discussed later. The amplitudes of the steps in the modulus of both L and T are higher than twice the amplitudes of the imaginary peaks, and this is due to broad distributions of the relaxation parameters. In fact, the overlapping of processes with different temperatures produces a step in the modulus whose overall amplitude is the sum of the amplitudes of the single components, whereas the height of the resulting peak of the imaginary part is smaller than the sum of the amplitudes of its components. Therefore, better estimates of the total relaxation intensities are deduced from the amplitudes of the steps in the modulus, $\frac{1}{2}\Delta Y/Y \sim 0.045$ for L and 0.08 for T in Fig. 5. These values are unusually high, especially if one considers that they are found in a stoichiometric material, and apparently do not occur in concomitance with structural phase transformations. In order to better appreciate this point, one should consider that a relative softening of 0.08 means that, on application of a tensile stress, the sample undergoes an additional extension of 8% due to the relaxation of the “defects.” For this reason, the relaxations L and T can only be accounted for by intrinsic mechanisms, which must be connected with the instability of the La_2CuO_4 lattice against certain types of deformations, like the tilting of the CuO_6 octahedra, and the large vibration amplitudes of the O atoms observed by neutron diffraction.⁶

Figure 6 presents the whole relaxation spectrum of sample 2, from 1.4 to 700 K both in the O doped and undoped conditions. The HTT to LTO transition occurs at 530 K in the undoped state, as expected, and at 500 K after the maximum oxygenation. According to the T, δ phase diagram of Zhou *et al.*,⁴ a transition temperature $T_{d1} = 500$ K corresponds to $\delta = 0.018$. The dissipation maximum just below

T_{d1} is typical of the movement of the domain walls created by the transformation from tetragonal to orthorhombic structure.³²

C. Relaxation T and the thermally activated flipping of CuO_6 octahedra

The main component of peak T in Fig. 3 has been fitted with $\tau_0 = 1.4 \times 10^{-12}$ s, $E/k = 2800$ K, $\alpha = 0.46$. It is considerably broader than pure Debye relaxation, and the attempt frequency is somewhat slower than that typical of atomic hopping. All these features are consistent with a coordinated motion of groups of atoms, like the proposed flipping of single CuO_6 octahedra or of a restricted number of them between configurations with different tilts and distortions. Since each octahedron shares the corners with the other four octahedra in the plane, the marked departure from pure Debye relaxation is a consequence of the static and dynamic interaction among these structural units.

However, the hypothesis that all the octahedra in the LTO phase may flip by thermal activation seems to be in contrast with the observation of static LTO domains with a long-range order. Actually, from a detailed neutron-diffraction study⁶ on single crystals of La_2CuO_4 and $\text{La}_{1.87}\text{Sr}_{0.13}\text{CuO}_4$ it results that the dynamic displacements of the O atoms in the directions of the tilts are even larger than the static ones at least down to 180 K, and remain comparable to the static displacements down to the lowest temperatures. This has been interpreted as a sign that the O atoms (particularly the apical ones) can switch configuration by thermal activation.⁶ The possibility that the relaxation processes L and/or T are directly related to the large dynamic displacements of O found by neutron diffraction is very attractive, and would also explain their extremely high intensities. Still, some care must be taken in directly identifying the dynamic displacements observed by neutron diffraction with the relaxation processes L and T, because the firsts are higher in the Sr-doped sample,⁶ while the intensity of the latter decreases with O doping. A direct comparison between the doping dependence of the Debye-Waller displacements and of the relaxation processes L and T cannot be made yet, due to the lack of complete spectra of the imaginary part of the elastic susceptibility of Sr-doped samples.

If the relaxational dynamics producing T does not involve the whole lattice, but only particularly unstable regions, these can be identified with the twin boundaries. Zhu *et al.*³ found that the transition between two twin LTO domains occurs smoothly through extended LTT- and HTT-like twin boundaries in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. These smooth domain walls can also be explained by constructing a model Landau free energy which reproduces the phase diagram of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and minimizing it along the twin boundary, with the tilt angles as order parameters.¹² These authors found that their model free energy has a local minimum for the LTT distortion also in undoped La_2CuO_4 .¹² Then, it is possible that also in La_2CuO_4 the domain walls are wide and unstable against the formation of the LTT or HTT phase, and peak T can be due to the thermally activated switching of entire octahedra between the two nearly energetically equivalent configurations.

Note that this mechanism should be distinct from the movement of the twin walls, which produce a dissipation

maximum at much higher temperature, slightly below the HTT-LTO transition at 500–530 K (Fig. 6).

D. Process L and the structural instability towards the LTT phase

Process L presents a less marked temperature shift with frequency, and it also occurs below 20 K, where suitably doped samples have passed into the LTT or *Pccn* phase. These facts, together with the high intensity indicating the involvement of a significant portion of the sample, suggest a connection with a phase transformation. Indeed, a comparable dissipation rise at such low temperatures can be found in the A15 compound Nb_3Sn ,⁴⁶ which undergoes a cubic to tetragonal transformation around 45 K; below that temperature, the elastic energy-loss coefficient becomes as high as 8×10^{-3} due to the stress-induced motion of the domain walls.⁴⁶

In La_2CuO_4 , peaks in the low-temperature ultrasound absorption have been attributed to the interaction of soft modes with the sound wave,⁴⁷ and a minimum around 40 K in the c_{66} in-plane shear⁴⁸ has been attributed to a relaxation process, possibly connected with the predicted highly anharmonic tilting mode of the apical O.⁴⁹ More data are available for the material with La partially substituted by Sr or Ba, where the new types of tilts are better stabilized, and the *Pccn* and LTT domains have actually been observed. In $\text{La}_{1.9}\text{Ba}_{0.1}\text{CuO}_4$ a step in the sound velocity was found at $T_{d2} = 50$ K (Ref. 34), when the LTO phase transforms into LTT, and in $\text{La}_{1.475}\text{Nd}_{0.4}\text{Sr}_{0.125}\text{O}_4$ two distinct dips in c_{66} were found at the transformations from LTO to *Pccn* and then to LTT.³⁵ In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, rises in the acoustic absorption and elastic constants have been frequently observed below 10–30 K, and attributed to the appearance of a new phase,^{34,50,51} to the occurrence of a glassy state³¹ or to other causes.^{33,47} In some cases no acoustic anomaly was observed below 60 K.^{52,53}

Nohara *et al.*⁵⁴ also studied the interplay between lattice instability and emergence of superconductivity. They found that $c_{66} [(c_{11} - c_{12})/2]$ in their HTT representation] starts softening below 50 K in $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$, and hardens again at the appearance of superconductivity; they could shift the onset of superconductivity and therefore extend the region of softening by applying a magnetic field. These observations have been interpreted as evidence of a structural instability of the LTO phase which is suppressed by superconductivity; the authors also noted that the in-plane shear strain coupled to the softening is responsible for a differentiation of the otherwise equivalent O atoms in the CuO_2 plane of the LTO phase, as for the LTT and *Pccn* phases.

The hardening found by us below 20 K has a nature different from that observed by Nohara *et al.*; in fact, it is maximum in the undoped sample, where superconductivity never sets in, and even in the highly doped state, with $T_c = 34$ K, there are no clear signs of the onset of superconductivity in the modulus. In addition, the variations of c_{66} in $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$ were below 0.3%, while the hardening in our undoped sample is up to 10%. This is shown in Fig. 7, presenting the susceptibility curves below 40 K for sample 2 from the completely outgassed state to the maximum O content that we can achieve; the decrease and shift to lower

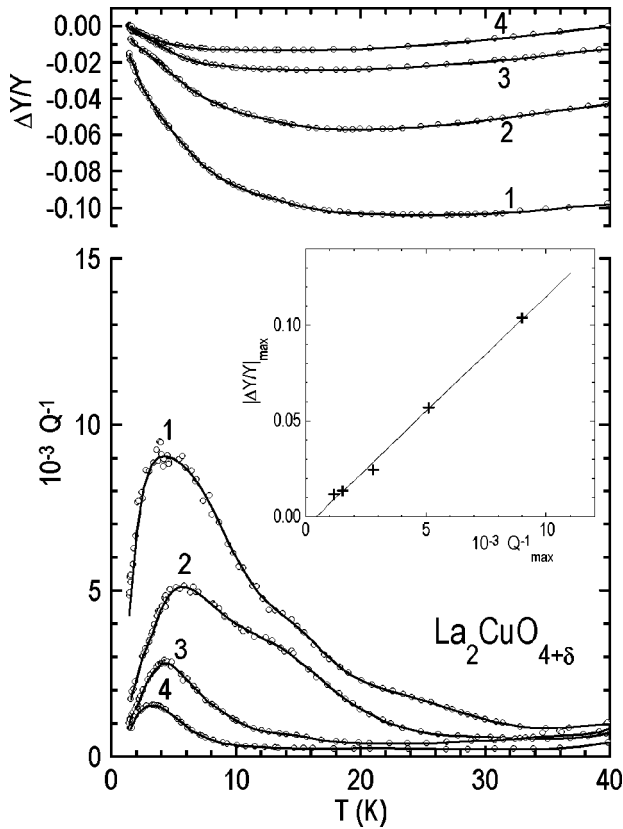


FIG. 7. Dependence of the relaxation process L on oxygen doping. Curve 1: outgassed; curves 2–4: equilibrated at 620 °C with 10, 1, and 0.7 torr O₂. The inset shows the linear correlation between the modulus step and the intensity of the absorption peak. The vibration frequencies at $T=0$ K were 510, 780, 840, and 890 Hz from curve 1 to curve 4.

temperature with O doping will be discussed in the next section. The inset also shows the linear correlation between the peak in the absorption and the negative step in the modulus, as expected from a relaxation process following Eq. (1); the reference values of Y were chosen in order that the extrapolations of $Y(T)$ coincide at $T=0$ K.

Still, the tendency to instability of the LTO phase is expected to play a role in a phenomenon which certainly involves a relevant fraction of the lattice. Since there are no signs of a precise temperature at which the acoustic dispersion starts, we interpret process L as relaxation among off-center positions created by the lattice instability toward the LTT-like tilts. Whether this can occur only in particularly disordered or unstable regions like the twin walls or also within the LTO domains, is a question connected with the issue whether the LTT phase propagates from the twin walls¹² or also nucleates in the LTO domains.¹³

The extremely broad shape of the $Q^{-1}(T)$ curves below 40 K and the fact that their shift to higher temperature at higher frequency is less marked than for the other processes, is not unusual at such low temperature, where the relaxation rate τ^{-1} is generally governed by quantum effects. Indeed, the broad shape of peak L cannot be reproduced with τ obeying the Arrhenius law for overbarrier hopping. We attempted to fit the $Q^{-1}(T)$ curves below 40 K by assuming hopping over two types of barriers, both with a distribution function whose width is up to half of its mean value, but also in this

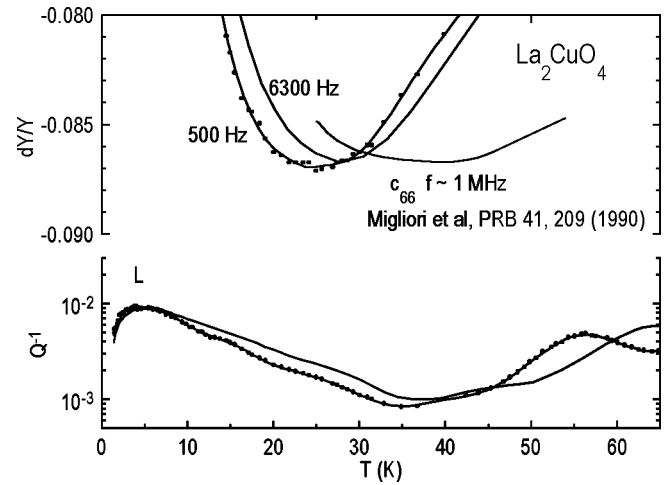


FIG. 8. Comparison between the measurements on our undoped ceramic La₂CuO₄ and the temperature dependence of c_{66} determined by Migliori *et al.* (Ref. 48) on a single crystal.

case the resulting curves consist of two well defined separate peaks, instead of the broad experimental curves. The only way to fit peak L by assuming overbarrier hopping with an attempt frequency of the order of the local atomic vibrations ($\tau_0 \sim 10^{-14}$ s) is to construct an *ad hoc* distribution of barriers $P(E)$ which is maximum around $E \sim 100$ K and has asymptotic behavior E^m and E^{-n} at low and high values of E , respectively, (the high-temperature side of the peak requires $n \sim 1.5$). A more physical picture is that the dynamics of relaxation L is dominated by tunneling. In fact, at progressively lower temperature the major contribution to τ^{-1} in a nonmetallic material comes from defect transitions involving two phonons and finally one phonon, which produce a temperature dependence much slower than the Arrhenius law ($\tau^{-1} \propto T^{-7}$ for two-phonon⁵⁵ and $\tau^{-1} \propto T$ for one-phonon processes⁵⁶). Then the shape of the $Q^{-1}(T)$ curve is also defined by the thermodynamic factor:

$$\frac{f_1 f_2}{T} = \frac{1}{T} \frac{c}{\cosh^2(A/2kT)}, \quad (2)$$

where A is the energy asymmetry between the two possible defect states, due to the nonequivalence of the configurations and to internal strains. The energy scale of the processes involving tunneling is comparable with the energy shifts A due to lattice disorder, causing a broadening of the relaxation function which further masks the temperature shift of the Debye function.

Support to the hypothesis that process L is of the relaxation type comes from the comparison of our measurements with those of Migliori *et al.*,⁴⁸ who reported the elastic constants of a La₂CuO₄ single crystal between 25 and 55 K. In Fig. 8 we put our data for stoichiometric La₂CuO₄, taken at 0.5 and 6.3 kHz, together with the temperature dependence of the c_{66} constant around 1 MHz;⁴⁸ c_{66} is the most sensitive to the distortions of the different phases of the 214 compounds, and is the most influential in determining the temperature dependence of the Young's modulus of the polycrystals.⁵⁷ The three curves $Y(T)$ and $c_{66}(T)$ are shifted in temperature according to the vibration frequency, as requested by the term containing $\omega\tau$ in Eq. (1). In addition, the

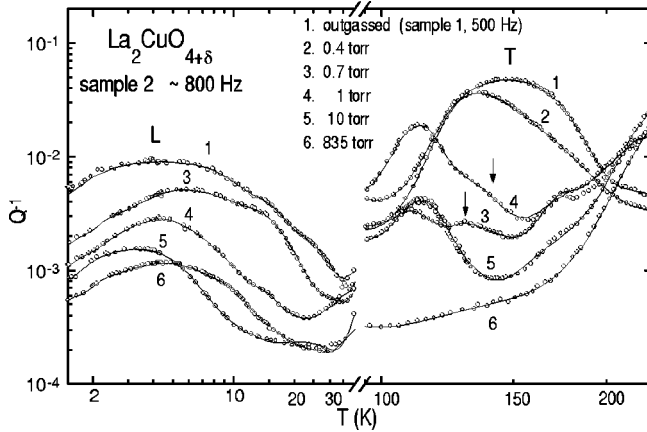


FIG. 9. Dependence of the relaxation processes L and T on oxygen doping. Curve 1: sample 1 after outgassing in vacuum at 750 °C for 75 min; curves 2–6: sample 2 after 1–2 h equilibration in a quartz tube with an initial O_2 pressure indicated in the legend. Peak T in curves 3 and 4 is indicated by an arrow, while the peak around 110 K in curves 4 and 5 is a different process, whose temperature is lower than that of peak T and does not shift with the O content.

Q^{-1} of the single crystal of Migliori *et al.* was reported to be of the order of 10^{-3} around 40 K and to increase at lower temperature, in perfect agreement with our ceramic samples. The same authors attributed the minimum of $c_{66}(T)$ to a relaxation process possibly connected with highly anharmonic phonon modes⁴⁹ or domain-wall motion.

E. Influence of doping

Figure 9 presents the evolution of the peaks L and T with increasing the O doping, $0 \leq \delta \leq 0.02$. Both peaks have a similar behavior under the introduction of small quantities of excess oxygen: they are depressed and shift to lower temperature, but peak T is much more effectively inhibited than peak L.

Also the partial substitution of La with Sr or Ba seems to inhibit these processes, but the data available in the literature are somewhat contradictory and insufficient to determine this issue. In addition, a direct comparison between low-frequency and ultrasound experiments is sometimes difficult, for example, due to the scattering of the sound waves from the domain walls in the latter type of experiments.

We try now to interpret this behavior of peaks L and T in terms of lattice disorder and electronic effects connected with the doping of charge carriers. It has been proposed⁴ that there is a mismatch between the bond lengths in the LaO planes and those in the CuO_2 planes, so that the CuO_2 planes are subjected to a compressive stress and become corrugated. This is considered as a cause of the tilting of the octahedra and therefore it has been identified as the driving force for the transition from HTT to LTO,⁴ although the observation of finite tilts also in the HTT phase¹⁶ indicates that the situation is more complex. Such a mismatch is described by the tolerance factor $t = [La-O] / \sqrt{2}[Cu-O] < 1$, which would be 1 in the case of stress-free flat planes. The introduction of interstitial O increases t for two reasons:⁴ (i) the interstitial atoms occupy tetrahedral sites between two

LaO planes, which therefore are expanded; (ii) the excess O^{2-} removes charge from the Cu-O antibonds,⁵⁸ so reducing the Cu-O bond lengths. High concentrations of excess O may even make t exceed 1 (Ref. 24) and similar effects are produced by the substitution of La^{3+} with the larger ion Sr^{2+} (Ref. 59). Let us now consider the double-well potential for the local atomic configurations which produce the anelastic relaxation T, whose separation between the minima represents the tilt amplitude. If these double potentials are partly due to the fact that $t < 1$, then a relief of the stresses between LaO and CuO_2 planes should result in a decrease of both the distance between the potential minima and of the barrier, i.e., in a decrease of the activation energy; a reduction of the average tilt angle of the octahedra with doping is actually observed.^{40,6} The reduction of the activation energy implies a faster rate for the hopping between the possible configurations and therefore the maximum of the anelastic relaxation intensity, which occurs around $\omega\tau = 1$, is shifted to lower temperature. The same argument holds for peak L, even if the relaxation dynamics is not describable by the classical rate theory; also when tunneling dominates, a reduction of the barrier results in faster rates and therefore in a shift to lower temperature of the corresponding relaxation process. We conclude that the introduction of holes in the CuO_2 planes reduces the barrier between the off-center configurations and therefore accelerates the relaxation dynamics.

On the other hand, the lattice disorder, both due to interstitial O and substitutional Sr and Ba, makes the double potentials more asymmetric. This results in a suppression of the relaxation when the induced asymmetry A is higher than kT , since the configuration with the highest energy is no more populated and the factor $f_1 f_2$ in Eqs. (1) and (2) goes to zero as $\exp(-A/kT)$. The fact that peak T is more markedly depressed than peak L is consistent with the hypothesis of a coordinated motion of entire CuO_6 octahedra; since the octahedra are correlated with each other, it is possible that the pinning due to a single interstitial oxygen propagates to several structural units, causing complete blocking already at low defect concentrations. Instead, the correlation is certainly lower for single O atoms making transitions between tunneling states.

The measurement with the highest content of excess O seems to contradict the above picture, because peak L in curve 6 of Fig. 9 is lower in intensity than curve 5, but shifted to higher rather than to lower temperature. This can be explained by the occurrence of the phase separation into O-rich and O-poor phases, with the O-rich phase not contributing to the relaxation process. In addition, it is possible that not all excess oxygen goes in the lattice as O^{2-} ions, but partly forms covalent bonds,^{24,38} for example O_2^{2-} pairs, which contribute less to the charge doping. Then, the unexpected shift to higher temperature of peak L at the highest O contents may be explained by the formation of covalent pairs which contribute only partially to doping, and therefore to the acceleration of the relaxation dynamics, but are effective in creating disorder and therefore in suppressing the intensity.

The conclusion that O atoms in $La_2CuO_{4+\delta}$ may tunnel and that their dynamics becomes faster on increasing doping poses the question whether this tunneling dynamics may play a role in the superconducting mechanism, since many models

have appeared of strong electron-lattice coupling mediated by tunneling states.^{60,61} Experimental evidences of double-well potentials along the z axis for the apical O atoms in 123 and Tl-based oxide superconductors have been provided mainly by extended x-ray-absorption fine-structure measurements,⁶² but are still controversial.^{63,64} In the present case there is evidence of an extraordinarily intense relaxation involving tunnel states, but it also seems that this relaxation mechanism loses importance at the doping levels at which the material becomes metallic and superconducting, at least for doping with interstitial O. Additional acoustic experiments may clarify this point.

IV. CONCLUSIONS

The present measurements show the existence of four anelastic relaxation processes in $\text{La}_2\text{CuO}_{4+\delta}$ which depend on the O stoichiometry and may reach very high intensities. Two of them are clearly connected with the presence of excess O, and from the analysis of the elastic energy loss peak due to hopping of single interstitial O atoms it has been possible to accurately determine their mobility.

It is also shown that, after eliminating the excess O, a relevant fraction of the lattice in the LTO phase presents relaxational dynamics on three different time scales, which is a manifestation of the intrinsic instability of the La_2CuO_4 lattice against certain types of deformations, like the tilting of the CuO_6 octahedra. This is in sharp contrast with Nd_2CuO_4 , which has a stable T' structure without CuO_6 octahedra and a flat dynamic elastic susceptibility. The

only transformation which is known to occur in undoped La_2CuO_4 is the HTT-LTO one, and the movement of the twin walls in the LTO domains cannot be responsible for three relaxation processes with widely different characteristic energies and temperatures (450, 150, and 5 K). The slowest relaxation, observed below the HTT-LTO transformation temperature, is attributed to the motion of the twin boundaries. The intermediate process, with relaxation times of the order of 1 ms around 150 K, is due to hopping over a barrier of ~ 0.23 eV; it is identified with thermally activated flipping of unstable CuO_6 octahedra, possibly in the domain boundaries, and is easily blocked by the lattice disorder introduced by excess oxygen. The faster relaxation motion, which is less effectively blocked by the interstitial excess O, has characteristic times of the order of 1 ms around 5–10 K and is dominated by quantum tunneling. It is proposed that the double-well potentials for the low-temperature relaxation are due to the tendency of the LTO phase to nucleate LTT domains. In stoichiometric La_2CuO_4 however, these domains cannot be stabilized, as in the doped lattice, by the mismatch between the sizes of the La ions and those which partially substitute it, or by the commensurate charge-density wave when doping is $\sim 1/8$. Therefore, possibly near the twin walls, the O sublattice can locally assume an LTT-like pattern, which however remains localized and short lived.

ACKNOWLEDGMENT

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