# Tilt-wave dynamics of the oxygen octahedra in La<sub>2</sub>CuO<sub>4</sub> from anelastic and <sup>139</sup>La NQR relaxation

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The anharmonic vibrational dynamics in nearly stoichiometric La<sub>2</sub>CuO<sub>4+ $\delta$ </sub> is studied by means of anelastic and <sup>139</sup>La NQR relaxation. In the absorption component of the elastic susceptibility as well as in the nuclear relaxation rate a peak is detected as a function of temperature, and a relaxation time  $\tau$ =1.7 ×10<sup>-12</sup> exp[(2800 K)/T] s is derived. The relaxation processes are attributed to tilt motion of the CuO<sub>6</sub> octahedra in double-well potentials, whose cooperative character increases the effective energy barrier to the observed value. The analysis of the relaxation mechanisms has been carried out by reducing the dynamics of the interacting octahedra to a one-dimensional equation of motion. The solitonlike solutions correspond to parallel walls separating domains of different tilt patterns and give rise to pseudodiffusive modes which appear as a central component in the spectral density of the motion of the octahedra. The tilt waves may be considered to correspond to the dynamical lattice stripes observed in La-based and Bi-based high- $T_c$  superconductors. [S0163-1829(99)04218-6]

## I. INTRODUCTION

There is growing interest in the local deviations from the average structure recently observed in cuprate superconductors. These local inhomogeneities are often identified with one-dimensional conducting domains of increased carrier density and antiferromagnetic carrier-depleted domains.<sup>1</sup> In some theoretical approaches such stripes are believed to play a role in the mechanism underlying high- $T_c$  superconductivity. Recently, the anelastic relaxation spectrum of undoped La<sub>2</sub>CuO<sub>4</sub> has been found to exhibit two intense relaxation processes, attributed to intrinsic relaxational dynamics of unstable lattice modes, namely quasirigid tilts of the O octahedra.<sup>2</sup> The relaxation process below 30 K is related to an instability toward the low-temperature tetragonal (LTT) structure, while the high-temperature process is thermally activated with an activation energy around 2800 K. In the present paper combined anelastic and <sup>139</sup>La NQR relaxation measurements of La<sub>2</sub>CuO<sub>4+ $\delta$ </sub> are presented and interpreted in terms of the collective dynamics of tilting CuO<sub>6</sub> octahedra in double-well potentials. The tilt waves can be considered the equivalent in the undoped system of the lattice stripes and structural inhomogeneities observed in high- $T_c$  superconducting oxides.

## **II. EXPERIMENTAL AND RESULTS**

The sample was a sintered bar  $45 \times 4.5 \times 0.5 \text{ mm}^3$  of La<sub>2</sub>CuO<sub>4+ $\delta$ </sub>; the excess O was extracted by outgassing at 750 °C down to an O<sub>2</sub> partial pressure of the order of  $10^{-8}$  torr. Such treatments can introduce few at. % of O vacancies

in the CuO<sub>2</sub> planes,<sup>3</sup> which are reversibly filled after reoxidizing at high temperature. These vacancies do not affect the anelastic or the NQR relaxation, being static at the temperatures of interest (below 500 K). The O stoichiometry in the as-prepared state is estimated<sup>3</sup>  $\delta \sim 0.004$ . Details on the sample preparation and characterization can be found in Ref. 2.

The elastic energy-loss coefficient  $Q^{-1}$ , measured by exciting the flexural vibrations, is given by  $S''(\omega)/S'(\omega) \simeq S''(\omega)/S(\infty)$ , where  $S(\omega)$  is the complex dynamic compliance, with unrelaxed value  $S(\infty)$ . The contribution to the imaginary susceptibility from a relaxation process with characteristic time  $\tau$  is<sup>4</sup>

$$Q^{-1} \propto [x(\delta \lambda)^2 / T] \omega \tau / [1 + (\omega \tau)^2], \qquad (1)$$

where x is the atomic fraction of relaxing entities, each producing a change  $\delta\lambda$  of the strain  $\varepsilon$  when its state changes;  $\omega/2\pi$  is the measuring frequency. The  $Q^{-1}(T)$  curve has a maximum at the temperature where  $\omega\tau(T)=1$ , yielding the relaxation rate at the peak temperature. The main processes appearing in the anelastic spectrum of La<sub>2</sub>CuO<sub>4+ $\delta$ </sub> above 100 K are due to the diffusive jumps of the interstitial O atoms. The peak attributed to the tilts of the O octahedra appears only after reducing the content of excess O down to very low levels ( $\delta$ <0.001). In fact the interstitial O atoms block the relaxational motion of several surrounding octahedra.<sup>2</sup> The anelastic peak in the nearly stoichiometric state is shown in Fig. 1 (left-hand scale). The two sets of data refer to the excitation of two flexural modes (460 Hz and 5.9 kHz). The peak due to O diffusion was 30 times smaller than

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FIG. 1. <sup>139</sup>La NQR relaxation rates  $W_Q$  (right-hand scale) and elastic energy loss  $Q^{-1}$  (left-hand scale) for a sample with  $\delta \sim 10^{-4}$ , after subtraction of the contribution from the O diffusion. Solid lines: best fits according to the model described in the text.

in the as-prepared state, indicating a concentration of residual oxygen  $\delta \sim 1 \times 10^{-4}$ ; such a small contribution has been subtracted in Fig. 1.

The <sup>139</sup>La NQR relaxation rate  $W_Q$  in the same sample is also shown in Fig. 1 (right-hand scale), again after subtraction of the contribution from the residual interstitial O which gives a monotonous increase of  $W_Q$  for  $T \ge 400$  K.<sup>8</sup> In  $La_{2-x}Sr_xCuO_{4+\delta}$  the <sup>139</sup>La NQR relaxation can be due to magnetic or quadrupolar mechanisms.<sup>5,6</sup> The magnetic relaxation is due to the fluctuation of the field at the La site, arising from the time dependence due to the Cu<sup>++</sup> spin operators. The quadrupolar mechanism is due to the fluctuation of the transverse components of the electric-field gradient at the La site, mainly caused by the vibrations of the surrounding O ions, or by a diffusing interstitial O atom passing close to the La nucleus. The two types of relaxation are described by different recovery laws,<sup>7</sup> so allowing the identification of the relaxation mechanism by irradiating different NQR lines. The coincidence in Fig. 2 of the recovery plots of the NQR echo signals at  $2\nu_Q$  and  $3\nu_Q$  ( $\nu_Q=3eV_{zz}Q/[2I(2I-1)]$  $\approx 6.2$  MHz, eQ is the <sup>139</sup>La quadrupole moment) for T



FIG. 2. Recovery plots of the amplitude of the free induction signal *M* after saturation of the  $3\nu_Q$  NQR line (closed symbols and solid lines) at 77 and 297 K. The open symbols are the recoveries corresponding to the irradiation of the  $2\nu_Q$  NQR line. The dashed and dotted lines are the curves expected in the case of pure quadrupolar and pure magnetic relaxation mechanisms, respectively.



FIG. 3. Relaxation rate  $\tau^{-1}(T)$  corresponding to the condition  $\omega \tau = 1$  at the maximum of the anelastic and NQR relaxation curves (Fig. 1). The slope of the straight line provides the effective activation energy  $E_{\rm eff}$ , which coincides with the mean activation energy of the best fit in Fig. 1.

>77 K indicate that above this temperature the mechanism is totally quadrupolar, i.e., due to the diffusion of interstitial O (subtracted in Fig. 1) and to the motion of the apical O atoms. The relaxation rate  $\tau^{-1}$ , determined from the condition  $\omega \tau = 1$  at the maxima of the  $Q^{-1}(T)$  and  $W_Q(T)$  curves, is plotted in Fig. 3 in logarithmic scale against the reciprocal of temperature. The three points can be closely fitted by a straight line  $\tau^{-1} = \tau_0^{-1} \exp(-E_{\text{eff}}/k_BT)$ ,  $\tau_0 = 1.9 \times 10^{-12}$  s and  $E_{\text{eff}}/k_B = 2800$  K, clearly indicating that the same process is observed by both techniques.

#### **III. DISCUSSION**

The relaxation character of the responses implies that the apical O atoms in the LaO planes perform pseudodiffusive motion in a strongly anharmonic potential. Such a potential should be associated with the softer lattice modes of the rigid-unit type, which are low-frequency modes involving relative rotations of rigid lattice units, with little or no distortion of the units (which would increase the restoring force and frequency of the mode). One can assume that the displacement of an apical O atom represents the rotation of the rigid octahedron, and both the anelastic and NQR relaxation are due to the switching of the octahedra between different tilts in multiwell potentials. Such potentials have been calculated for La<sub>2</sub>CuO<sub>4</sub> (Ref. 9) and optimally doped  $La_{2-x}Ba_{x}CuO_{4+\delta}$  (Ref. 10) and  $La_{2-x}Sr_{x}CuO_{4+\delta}$ .<sup>11</sup> Minima were found for tilts corresponding to displacements of the apical O atoms by  $\delta \sim \pm 0.2$  Å in the [110] directions (parallel to the in-plane CuO bonds), corresponding to the low-temperature orthorhombic (LTO) structure, separated by an energy barrier of E=35-53 meV (400-600 K). Additional minima are found in correspondence to the lowtemperature tetragonal (LTT) structure with tilts about the [100] directions,<sup>9</sup> but the LTT domains can be observed by diffraction experiments only when doping around  $\frac{1}{8}$  by Ba or combined Sr and Nd substitution.<sup>12</sup> In the following both the anelastic and NOR measurements are interpreted in terms of cooperative motion of the octahedra in such multiwell potentials.

Let us first consider the <sup>139</sup>La NQR relaxation due to the atomic displacements s(t) of the apical O atoms surrounding the La nucleus. In order to simplify the interpretation, we will assume uncorrelated motion of such atoms, and approximate the relaxation rate  $W_Q$  in the form<sup>13</sup>

$$W_{Q}(\omega) \simeq a \left(\frac{eQ}{\hbar}\right)^{2} \left(\frac{\partial V_{zz}}{\partial s}\right)^{2} \int \langle s(t)s(0) \rangle e^{-i\omega t} dt = A^{2} \cdot J(\omega),$$
(2)

where *a* is a constant of the order of  $5/8I \approx 0.178$ ,  $\langle s(t)s(0) \rangle$  is the autocorrelation function of the motion of the apical oxygen, and  $J(\omega)$  the corresponding spectral density. If s(t) can switch between two values  $\pm \delta$  corresponding to two tilt orientations with probability  $1/(2\tau)$ , then the correlation function is  $\langle s(t)s(0) \rangle = \delta^2 e^{-|t|/\tau}$  and the NQR rate becomes

$$W_Q = A^2 \,\delta^2 2 \,\tau / [1 + (\omega \,\tau)^2], \tag{3}$$

where  $\tau$  is the correlation time.

The imaginary part of the elastic compliance  $S''(\omega)$  can be expressed in terms of the spectral density of the autocorrelation function of the macroscopic strain  $\varepsilon(t)$  (Ref. 14),

$$S''(\omega) = (\omega V/2k_{\rm B}T) \int \langle \varepsilon(t)\varepsilon(0) \rangle e^{-i\omega t} dt, \qquad (4)$$

*V* being the sample volume. In the assumption that  $\varepsilon(t)$  is directly related to the displacements s(t) of the O apical atoms, Eqs. (1) and (4) differ from Eqs. (2) and (3) only by a factor  $\omega/T$  and by the constants expressing the dependence of strain and NQR frequency on the atomic displacements.

Now it must be explained why the apparent activation energy  $E_{\rm eff}$  for the switching rate  $\tau^{-1}$  is higher than the theoretically estimated local potential barrier  $E^{9-11}$  This is related to the cooperative character of the motion of the octahedra, which has been widely discussed by Markiewicz.<sup>15</sup> He considered an LTT ground state and observed that, neglecting intraplane interactions, the octahedra along directions perpendicular to the tilt axes are strongly correlated, since they share the O atoms which are displaced from the CuO plane, while adjacent rows are weakly correlated, since the shared O atoms remain in the CuO plane. The system is thus reduced to a one-dimensional array of rows of octahedra, where all the octahedra belonging to the same row are tilted according to the same pattern. The resulting equations of motion are nonlinear and admit solitonic solutions, which correspond to one-dimensional propagating walls between domains with different tilt patterns.<sup>15</sup> This analysis allows one to apply the one-dimensional models of nonlinear lattice dynamics which have been used to describe structural phase transformations,<sup>11</sup> as well as the correlated dynamics of offcenter atoms in perovskites.<sup>16</sup> One can consider a potential of the form  $V = \sum_{i} - as_{i}^{2} + bs_{i}^{4} + \overline{c}s_{i}s_{i+1}$ , where each atom moves in two minima separated by an energy barrier E $=(a^2/4b)$  with a bilinear coupling to the neighbors. The coupling constant  $\overline{c}$  takes into account a cluster average over configurations. The resulting equation of motion has solitonic solutions similar to those found for the octahedra in  $La_2CuO_4$ ,<sup>15</sup> and it can be proved<sup>16</sup> that the spectral density  $J(\omega)$  contains both a resonant peak at the frequency of vibration in each well, and a central peak of pseudodiffusional

character with characteristic frequency  $\tau^{-1} = \tau_0^{-1} \exp(E_{\text{eff}}/T)$  with  $E_{\text{eff}} \approx 1.75E \sqrt{2c/a}$ ,  $\tau_0 = d/v \sqrt{c/a}$ , where v is the average velocity of propagation of the solitonlike excitation through the atoms spaced by d. These solitonic solutions provide the observed relaxational contribution to the spectral density and susceptibility. The effective potential barrier  $E_{\text{eff}}$  is increased with respect to the local barrier E by the interaction between the octahedra.

In fitting the experimental data with the above model, a distribution of the values of  $\overline{c}$  has been introduced, corresponding to the distribution in size and shape of the regions where the octahedra clusters build up the cooperative dynamics. Such regions are limited by the excess O atoms, which block the relaxational dynamics. The interaction parameter  $\overline{c}$  was distributed according to a Gaussian, resulting in a distribution of effective energy barriers  $E_{\rm eff}$ .

A feature of the anelastic peak which cannot directly be accounted for by the above formulas is the increase of its intensity at higher temperature, instead of a decrease as expected from Eq. (1). Such a temperature dependence is observed in the case of relaxation among states which differ in energy by  $\Delta E \ge k_{\rm B}T$ . In this case the relaxation strength must be multiplied by a factor containing the product of their equilibrium occupation numbers,<sup>17</sup>  $4n_1n_2 = [\cosh(\Delta E/2k_BT)]^{-2}$ This causes a decrease of the relaxation strength below T $\sim \Delta E/k_{\rm B}$ . The relaxation rate must be multiplied by  $\cosh(\Delta E/2k_{\rm B}T)$ , but this correction does not affect sizably the relaxation curves. The expression of the NQR rate should be modified in the same manner.<sup>18</sup> It should be remarked that these corrections are strictly valid for relaxation between levels without cooperative effects, and their extension to the above model of cluster dynamics is not obvious.

The resulting fit is shown in Fig. 1 as continuous lines. The mean values  $\tau_0 = 1.7 \times 10^{-12}$  s and  $E_{eff} = 2800$  K are the same as deduced from the condition  $\omega \tau = 1$  at the maxima (Fig. 2). The effective barrier  $E_{eff}$  is compatible with the theoretically estimated<sup>9-11</sup> local barrier of ~500 K with a mean coupling constant  $\bar{c}_0 \approx 5a$ . The width of the distribution of  $\bar{c}$  is  $\sigma = 0.18\bar{c}_0$  for the NQR and  $0.25\bar{c}_0$  for the ane-lastic data (a temperature-dependent width may result from the ordering of interstitial O); the resulting distribution in  $E_{eff}$  is Gaussian with a width of ~300 K. The asymmetry energy  $\Delta E = 280$  K is 10 times smaller than  $E_{eff}$  and therefore it does not affect the overall picture.

The fit value for the strength of the NQR relaxation mechanism is  $A \cdot \delta = 74$  kHz; *A* can be estimated in the hypothesis of independent displacements of the O atoms, assuming  $\partial V_{zz}/\partial s = 3V_{zz}/d$  (d = 2.7 Å is the La-O distance), and for  $\delta \sim 0.2$  Å it yields a relaxation strength  $A \cdot \delta = (3 \omega_Q/d) \delta \approx 8.6$  MHz, about a factor 100 larger than the experimental one. A reduction of the strength of the relaxation mechanism may be due to the correlation between the displacements of the five apical O atoms surrounding the La nucleus, giving rise to a form factor which multiplies the spectral density. This correction, however, can hardly produce a reduction by 100 times, which is likely to reflect the fraction of octahedra which are instantaneously changing the tilt orientation. In a simple picture one can consider independent solitonic domain walls (DW's), corresponding to tilt

waves which propagate through the lattice with velocity v; each La nucleus contributes to the NQR relaxation only when run over by the tilt wave, so that the relaxation strength should be reduced by the fraction of octahedra within the domain walls.

Along the same line, one could attribute the observed increase of the anelastic relaxation intensity with temperature to a temperature-dependent volume fraction of DW's, instead of introducing the asymmetry energy  $\Delta E$ . An increase of DW density, roughly as  $(T_t - T)^{-1}$ , is indeed observed on approaching martensitic transformations,<sup>19</sup> but is not sufficient to explain the increase of the anelastic relaxation strength by 30% from 147 to 170 K [Fig. 1, taking into account the 1/T factor in Eq. (1)]. In the present case, the DW's exist below the transformation from the high-temperature tetragonal structure to the LTO structure at  $T_t = 530$  K and their density would increase only 6% on increasing the temperature from 147 to 170 K.

From the close coincidence of the relaxation rate describing the anelastic and NQR results, it is deduced that the propagation of solitonlike walls is the origin of both types of relaxation, and that there is a direct relationship between the atomic displacement *s* and macroscopic strain  $\varepsilon$  whose spectral densities are probed by the two experiments. Such a direct relationship can be assumed for the movement of a wall separating two LTO domains with opposite signs of the in-plane shear strain  $\varepsilon_{xx} - \varepsilon_{yy}$  (in LTO notation, with *a* and *b* directions at 45° with the CuO bonds). The propagation of such DW changes the domain sizes and therefore modulates  $\varepsilon$ .

The spatial arrangement of the domains of tilted octahedra cannot be deduced by our data, but the above analysis corresponds to an array of propagating parallel fronts of tilt waves. Similarly, the picture proposed by Markiewicz<sup>15</sup> for  $La_{2-x}Sr_xCuO_{4+\delta}$  is a LTT ground state with lowest energy excitations consisting of parallel propagating LTO walls. A closely spaced structure of alternating LTT domains and propagating LTO walls would form a so-called dynamic Jahn-Teller phase with average orthorhombic structure, and

conventional diffraction measurements would see the average structure (the intermediate structure between two LTO domains is LTT and vice versa). Such a microstructure closely corresponds to the lattice stripes proposed by Bianconi et al. on the basis of extended x-ray-absorption finestructure results in the same doped material  $La_{1.85}Sr_{0.15}CuO_{4+\delta}$  (Ref. 20) and in  $Bi_2Sr_2CaCu_2O_{8+\nu}$ .<sup>1</sup> Stripes have also been observed by neutron diffraction<sup>21</sup> in  $La_{1,6-x}Nd_{0,4}Sr_{x}CuO_{4}$  with x=0.12, where they are pinned by the formation of a stable LTT structure. Also our <sup>139</sup>La spectra exhibit asymmetric broadening of the lines split by the local magnetic field observed by other authors,<sup>22</sup> supporting the picture of channels where the charges doped by the residual excess O are mobile and depress the antiferromagnetic order.

### **IV. CONCLUSION**

In summary, thermally activated relaxation processes due to strongly anharmonic lattice modes have been evidenced in nearly stoichiometric  $La_2CuO_{4+\delta}$  from the elastic susceptibility and <sup>139</sup>La NQR relaxation rate versus temperature, as a low-frequency tail of the spectral density of the atomic motions. The pseudodiffusive motions have been identified as the tilt modes of the O octahedra in a multiwell potential. In the interpretation, we have used the fact that the dynamics of the octahedra in the ab plane can be cast into a nonlinear one-dimensional equation, which admits solitonic solutions corresponding to propagating walls between domains with different tilt patterns. Thus it has been possible to rely on the analysis of similar one-dimensional systems, for which the spectral density contains a pseudodiffusive central peak of width  $\tau^{-1} = \tau_0^{-1} \exp(-E_{\text{eff}}/k_{\text{B}}T)$  related to the solitonlike lattice excitations. The measured effective barrier  $E_{\rm eff}/k_{\rm B}$ = 2800 K is about five times higher than the barrier of the theoretically estimated local potential, due to the cooperative character of the motion. The alternating LTO domains and LTT walls should correspond to the lattice stripes observed in superconducting oxides.

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