PHYSICAL REVIEW B VOLUME 45, NUMBER 2 1 JANUARY 1992-II

Low-temperature phase transformations in $YBa_2Cu_3O_{6+x}$ by anelastic relaxation measurements and possible formation of ferroelectric and antiferroelectric domains

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(Received 18 July 1991; revised manuscript received 16 September 1991)

We report on three phase transformations occurring between 120 and 170 K in $YBa_2Cu_3O_{6+x}$ for $x > 0.2$. It is proposed that one or two of them are due to the ordering of the O atoms among the off-center positions in the Cu-O zigzag chains. Since an electric dipole is associated to O^{2-} ions in such off-center positions, ferroelectric (oxygens on the same side of the chain) and antiferroelectric (oxygens on opposite sides in zigzag fashion) domains should also form. The proposed interpretation correlates well with the overall phenomenology, including an anelastic relaxation process previously interpreted in terms of the nearly uncorrelated jumps of such oxygens. The phase transition around 170 K may correspond to a ferroelectric displacive transition appearing in the dielectric function.

INTRODUCTION

The $YBa_2Cu_3O_{6+x}$ ceramic has a rich and mostly unexplored phase diagram in the (x,T) plane, and, due to the unusually high mobility of O in the CuO_x planes,[1,2] O ordering has been observed to take place also at room temperature, drastically influencing the superconductive properties of O-deficient samples.[3,4]

A phase transition occurring around 230 K has been attributed to O ordering in the basal planes,[5] because of its coincidence with reversible twin refinements,[6] which imply jumps of the O atoms between the O(1) and O(5) positions in the CuO_x planes. However, it is unlikely that all the observed phase transitions are connected to reordering of O between O(1) and O(5) positions. This is especially true for those transitions occurring below 200 K in samples with $x \sim 1$, where it is presumed that most of the material is in the ortho-I phase and there is little possibility for further ordering.

In superconducting $YBa_2Cu_3O_{\sim 7}$ ferroelectric phase transitions have been revealed at 90 and 170 K by measuring the dielectric constant through the ultrasound-induced rf field.[7] Coexistence of ferroelectricity, presumably in the CuO_x planes, with metallic conductivity and superconductivity in the CuO_2 planes may be of relevance for the coupling mechanism which leads to superconductivity.

On the other side, an anomaly around $T_t \sim 110-130$ K (subscript t stands for "transformation") has been observed by acoustic measurements both at kHz (Refs. 8-10), and the MHz (Ref. 11), and by a jump in the lattice parameters by x-ray diffraction measurements.[8,12] Such an anomaly has been attributed to a martensiticlike phase transition,[8-11] and put in close connection with the 92 K superconductivity.[8-11] It has been argued that the state below T_t is the true normal state which becomes superconducting;[11] moreover, it has been suggested that superconductivity could arise from the lattice instability associated with the phase transition at T_t, similarly to the case of the $A15$ superconductors.[8-10] Such an anomaly at $T_t \sim 120$ K has been reported to disappear in concomitance with the disappearance of the 92-K superconductivity, and a new elastic anomaly at 70 K has been observed to be connected with the 60-K superconductivity.[10] Similar results have been obtained regarding the 107-K and 83-K superconductivity in Bi-Sr-Ca-Cu-O and the 115-K superconductivity in Tl-Ba-Ca-Cu-O, thus pointing to superconductivity induced by a structural instability.[8-10]

On the other hand, in most experiments there is no trace of the 110-130 K elastic anomaly; moreover, at vibration frequencies in the kHz range at which most experiments are conducted, the anomaly occurs at a temperature close to that of a thermally activated process, which also disappears in O-deficient samples,[13] so that it is possible to confuse the two processes.

We conducted additional anelastic relaxation experiments in order to clarify the phenomenology of the phase transitions below 200 K. We also propose an interpretative model based on the existence of off-center positions of the O atoms in the Cu-O zigzag chains. The model takes into account the thermally activated hopping and the possible ferroelectric and/or antiferroelectric ordering of the O atoms in such off-center positions.

EXPERIMENTAL

The samples were rectangular bars (44 mm long and 0.2–1.1 mm thick) prepared from a solid state reaction, according to a procedure described elsewhere.[14] The starting O content was varied between $x = 0.92$ and $x = 0.35$ by thermal treatments in vacuum. The O stoichiometry was estimated by the cell parameters obtained by x-ray diffraction,[15] and further checked by titration; the estimated error in its determination is ± 0.05 per formula unit.

The elastic energy dissipation, Q^{-1}, and the resonant frequency (whose square is proportional to the modulus) were measured between 50 and 300 K by exciting electrostatically the 1st and 5th flexural vibration modes of the bars. Both modes could be excited during the same experiment, so allowing an easy distinction between the thermally activated processes, which shift to higher temperature when increasing frequency, and those connected to phase transformations, whose position in temperature is nearly frequency independent.

RESULTS

The main features of the phase transitions between 120 and 170 K are shown in Fig. 1, where the concomitant measurements at two vibration modes (660 and 8600 Hz) of a same sample are reported. The sample, with $x = 0.35$, did not display the superconducting transition down to 35 K, and Fig. 2 is representative of the resistivity of all the specimens from the same batch. During cooling only a step in the modulus around 85 K is observed, and the peak labeled as $P3$ at 82 K (91 K at 8600 Hz) is due to a thermally activated process, possibly connected with jumps of the O atoms between off-center positions in the Cu-O chains[13] or to some low-energy excitation.[16] After aging for 20 h below 80 K, peak $P3$ is closely retraced during the slow heating, and sharp anomalies appear both in modulus and dissipation, which we call $PT1$, $PT2$, and $PT3$. Process $PT1$ consists in a sharp dissipation peak around 122 K and in a kink of the modulus, coinciding with the onset of the Q^{-1} rise; $PT2$ is a step of the Q^{-1} at 151 K, and $PT3$ is a kink in the modulus around 169 K. All three processes are nearly frequency independent both in temperature (thus denoting a phase transition) and in amplitude.

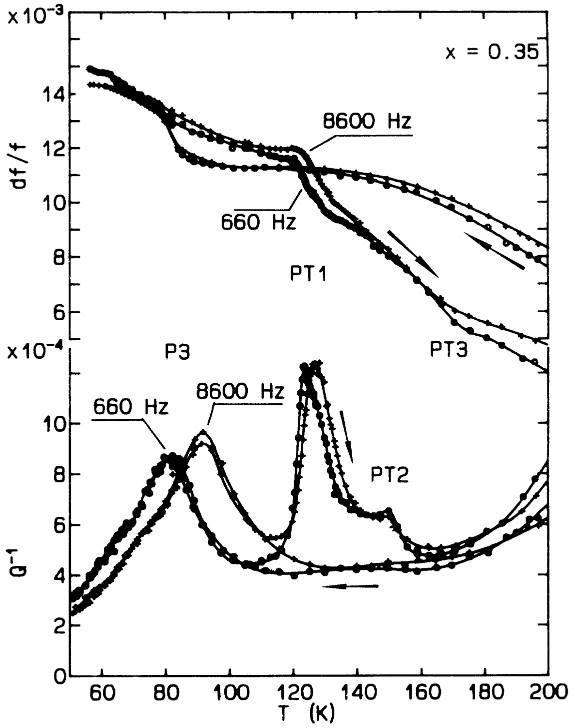

FIG. 1. Elastic energy dissipation Q^{-1} and relative variation of the resonant frequency of $YBa_2Cu_3O_{6.35}$ measured at two resonant frequencies on cooling and subsequent heating.

Figure 3 shows analogous measurements on samples with different O contents, from $x = 0.92$ to $x \sim 0.3$. For clarity, only the heating runs and one frequency per run are shown. During the corresponding cooling runs, only the thermally activated processes, $P2$, $P3$ and $P4$, and sometimes the modulus step around 85 K were observed, and the arrows indicate the frequency-independent effects $PT1$, $PT2$, and $PT3$.

Although the latter three processes do not appear always in the same way, and there is no obvious correlation

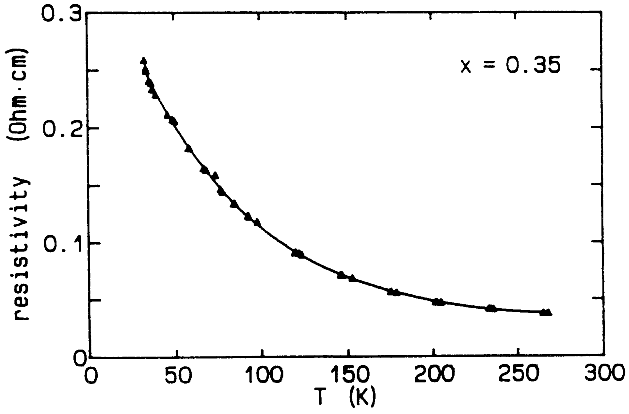

FIG. 2. Resistivity of a sample from the same batch of the sample of Fig. 1, with $x = 0.35$.

between their intensity and the value of x, they have a common feature: they only appear on heating, after a few hours of aging below 90 K. Measurements were repeated on the sample with $x \sim 0.55$, limiting cooling to temperatures above 100 K: neither $PT1$ nor $PT2$ were observed [Fig. 4(a)]. Instead, after aging below 80 K $PT1$ appears [Fig. 4(b)] and its intensity gradually decreases during thermal cycling around its temperature [Fig. 4(c)].

Figure 5 presents four measurements on the sample of Fig. 1, after subsequent O outgassing treatments in vacuum, starting from $x = 0.35$; below that value of x, the intensity of $PT1$–$PT3$ gradually vanishes.

The evolution of the thermally activated peaks $P2$, $P3$, and $P4$ with varying x has been discussed in Ref. 13, and can be briefly summarized as follows. When O outgassing proceeds starting from $x \sim 1$, $P4$ gradually decreases and disappears around $x \sim 0.5$; concomitantly, $P3$ slightly rises for x down to ~ 0.4. Peak $P2$ appears below $x \sim 0.3$ and becomes soon much higher than $P3$, which possibly coexists with it or disappears. Peak $P2$ has been attributed to the hopping of the isolated O atoms left in the O depleted CuO_x plane,[1,2] having an activation energy of 0.11 eV.

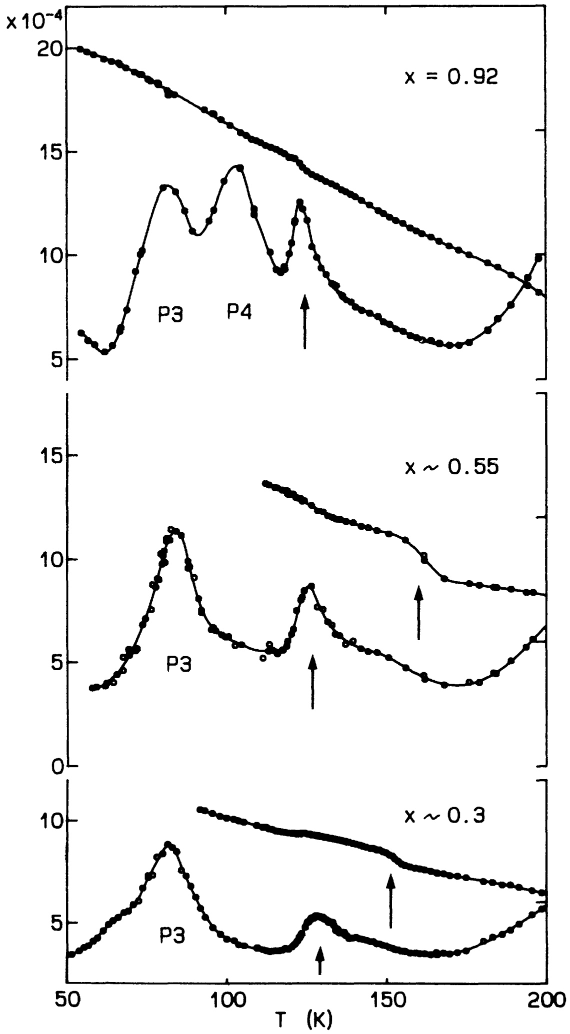

FIG. 3. Elastic energy dissipation Q^{-1} and relative variation of the resonant frequency of a series of samples $YBa_2Cu_3O_{6+x}$ with different values of x. All the curves are measured on heating, after aging ~20 h below 80 K.

DISCUSSION

We suppose that the elastic anomalies around 130 K presently reported, mainly $PT1$, correspond to those mentioned in Refs. 8–12. We note, however, that when $x > 0.6$, it is not easy to distinguish $PT1$ from $P4$ by resonant bar measurements, because at frequencies of several kHz the latter occurs at nearly the same temperature. The dissipation curve measured at 480 Hz of Fig. 6 is a case in which $PT1$ is particularly well separated from $P4$, because of the low measuring frequency. Also, the steps and kinks in the moduli may be masked by the large hysteresis due to the phase transition at 230 K, attributed to O ordering in the CuO_x plane,[5] whose amplitude and shape strongly depend on the microstructure and thermal history of the sample.[5,17,18]

Two new aspects appear from the present measurements: (i) nothing is observed on cooling without a previous aging below 100 K; (ii) $PT1$ is present also when the material is semiconductorlike down to 35 K. Both obser-

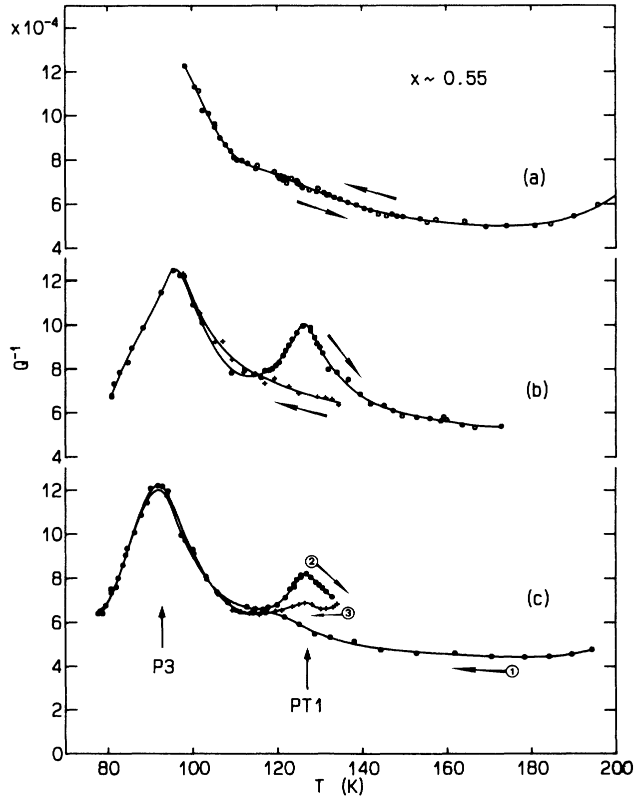

FIG. 4. Dependence of $PT1$ and $PT2$ on thermal cycling; (a) cycles above 100 K, starting from room temperature; (b) cooling below 80 K and corresponding heating on the same sample; (c) cooling from room temperature below 80 K (1), heating just above $PT1$ (2), and subsequent cooling (3).

vations indicate that the possible connection of the 130-K phase transition *PT*1 with the 92-K superconductivity is not so obvious as in the *A* 15 superconductors.

On the other hand, we note a surprising similarity between the phenomenology displayed by *PT*1-*PT*3 and the ferroelectric phase transitions reported at 90 and 170 K.[7] In fact, the dependence on thermal cycling summarized in Fig. 4 applies to both cases: the phase transitions are observed only on the heating following aging below 90 K and after that, they can be shortly observed also on cooling. Moreover, in both cases they are best observed in samples having a large hysteresis in the elastic constants below 230 K; this denotes a dependence on the microstructure, i.e., grain size, twin density, and microscopic distribution of the preexistent phases. Apparently the long aging times required indicate that the formation of the new domains proceeds against the constraint of the surrounding matrix. Accordingly, a large hysteresis in the moduli implies an easier motion of the domain walls (twins) and therefore an easier formation of domains of different phases.

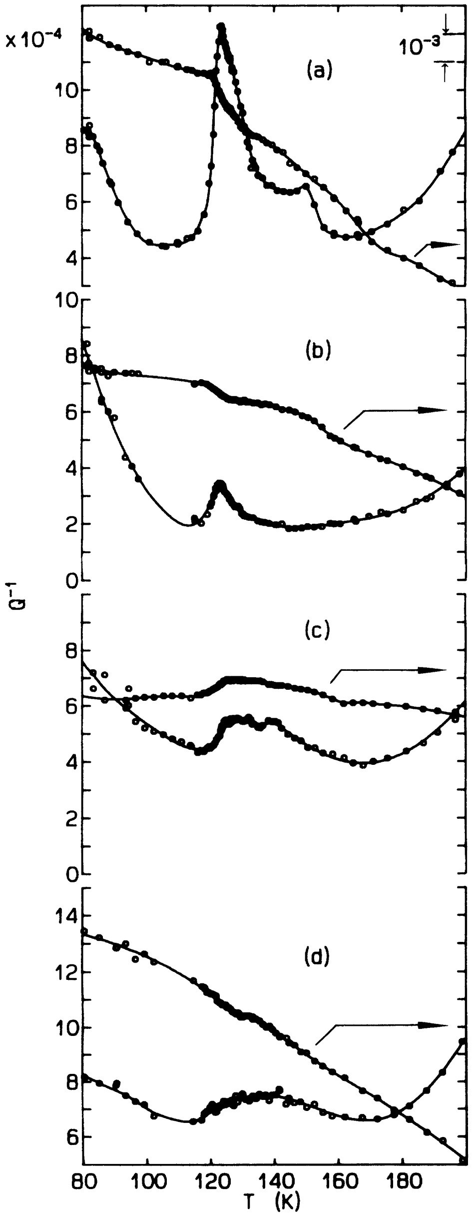

FIG. 5. Gradual disappearance of *PT*1-*PT*3 (measured on heating after aging below 80 K) due to high-temperature outgassing treatments in vacuum; (a) starting value of $x=0.35$; (b) after heating up to 810 K; (c) after aging at 990 K for 2 h; (d) after subsequent aging at 1000 K for 2 h.

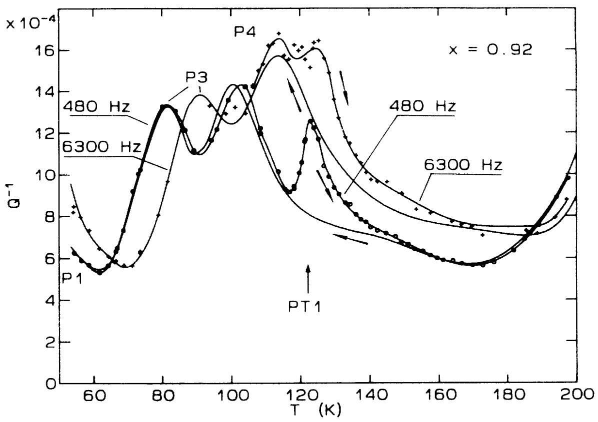

FIG. 6. Elastic energy dissipation of $YBa_2Cu_3O_{6.92}$ measured at two resonant frequencies on cooling and subsequent heating. *PT*1 and *P*4 overlap and are separated only at the lowest frequency.

Also due to such a scarce reproducibility from sample to sample, it is not always possible to distinguish unambiguously *PT*2 from *PT*3, when only one of the two transitions is clearly present; nonetheless, it seems reasonable to identify *PT*3 with the 170-K ferroelectric phase transition reported in Ref. 7, even though those measurements were not extended to O-deficient samples. The elastic counterpart of the 90-K ferroelectric phase transition is more difficult to discern; several papers report on jumps or kinks in the elastic constants of poly-crystals and single crystals around 90 K.[19–21] They generally relate those anomalies to the onset of superconductivity, even though they may be of the wrong order of magnitude and sometimes of the opposite sign, with respect to what is expected for the normal-superconductor transition.[19–21] We also measured sometimes such anomalies around 90 K, also on cooling from room temperature, but they are nonreproducible and much less evident than *PT*1–*PT*3; the modulus step around 85 K in Fig. 1 is an example of such effects. They could be due to the formation of the domains giving rise to *PT*1 on heating, even though a contribution of the 90-K ferroelectric transition[7] is possible.

Before proposing a model for *PT*1 and *PT*2, we summarize the experimental data concerning the low-temperature phase transitions. Four distinct anomalies in the elastic properties can be observed between 90 and 170 K, and at least two in the dielectric function. In the oxygenated material at 90 K the dielectric function denotes the occurrence of a ferroelectric transition of resonant type, i.e., due to the softening of a polar optical phonon mode.[7] At about the same temperature, anomalies in the elastic constants have been often reported which may be partly correlated with the ferroelectric transition, rather than to the superconductive one.[18–21] Between 120 and 150 K, two more transitions, *PT*1 and *PT*2, are revealed by both the elastic energy dissipation and modulus. *PT*1 has been interpreted as a martensitic-type transition,[8–10] i.e., small permanent shifts of the equilibrium positions of some atoms, due to the softening of an optical mode, similarly to the 90-K displacive transformation. An additional step in the elastic modulus, *PT*3, may appear around 170 K; this is the same temperature of the second ferroelectric transition as revealed by the dielectric function, again of resonant type.[7] The three phase transitions *PT*1, *PT*2, *PT*3 appear only after aging below 90 K; they are present from $x \sim 1$ down to $x \sim 0.3$ and gradually disappear below that O concentration.

ORDERING OF THE O ATOMS AMONG THE OFF-CENTER POSITIONS IN THE Cu-O CHAINS.

It seems established that the O atoms in the Cu-O chains do not occupy exactly the O(1) positions at $(0,\frac{1}{2},0)$, but slightly off-center positions $(\pm\delta_x,\frac{1}{2},0,)$ with $\delta_x \sim 0.15$ Å nearly independent of temperature both in oxygenated[22,23] and O-deficient samples.[24] This zigzag configuration would be dynamic, with a relaxation time $> 10^7$ s.[23] Also, a larger shift of the same O atoms in the c direction, i.e., $(0,\frac{1}{2},\pm\delta_z)$, with $\delta_z \sim 0.4$ Å has been observed, particularly in samples with low O content.[25] In Ref. 13 we discussed in detail the possibility that *P*4 and perhaps *P*3 are the anelastic relaxation processes associated with the O jumps between such off-center positions; there, we discussed the O jumps between the off-center positions in the a direction, but the same holds for the possible off-center positions along the c direction. An O atom jumping from $(\delta_x,\frac{1}{2},0)$ to $(-\delta_x,\frac{1}{2},0)$ and *vice versa* will couple both to electric and strain fields. In the first case the jump reverses the electric dipole associated with the O^{2-} ion in the chain. On the contrary, strain is centrosymmetric, and therefore the elastic dipole,[26] i.e., the local strain, associated with a single O remains unaffected by its jump, and one should consider chain segments containing two O atoms, rather than single O atoms.[13] There are two types of chain segments: those of type 1 joining O atoms on opposite sides with respect to the chain (one at δ and the next at $-\delta$) and those of type 2 joining O atoms on the same side (both at δ or $-\delta$), as shown in Fig. 7. The elastic dipoles λ^1 and λ^2 associated with them have different components, due to their different symmetry. A jump of an O atom belonging to two segments of the same type transforms them into the other type [Fig. 7(a)], thus changing their contribution to strain of $\pm 2(\lambda^1-\lambda^2)$; instead, a jump of an O belonging to two segments of different type simply exchanges them [Fig. 7(b)] and does not couple to strain.

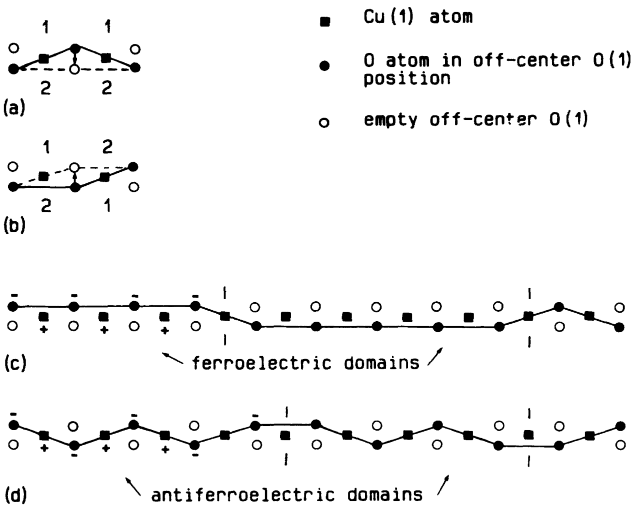

FIG. 7. Schematic representation of the zigzag Cu-O chains; (a) jump of an O atom belonging to segments of the same type and giving rise to a change in the local strain; (b) jump of an O atom which does not affect the local strain; (c) chain with ferroelectric domains; (d) chain with antiferroelectric domains.

In Ref. 13 we discussed the anelastic relaxation resulting from such jumps, neglecting any interaction among the O atoms. We now consider the possibility that, due to elastic and electric interactions, they may order in ferroelectric or antiferroelectric domains, as shown in Fig. 7. This closely resembles the case of order-disorder ferroelectrics, as, e.g., $NaNO_2$.[27] Such materials are paraelectric when the ions are equally distributed in a disordered manner between the possible off-center positions, and may undergo ferroelectric or antiferroelectric transitions when the ions order themselves among such off-center positions. This type of transformation differs from the displacive transformation; the latter one is driven by the instability of a soft polar optic mode, and results in finite permanent displacements of the atoms to a structure of lower symmetry.[27] The purely elastic counterpart of a displacive transition is a martensitic transition, as proposed for *PT*1 in Refs. 8–11.

The possibility of ferroelectric ordering of the oxygens in the zigzag chains has been already expressed by Müller and Maurer;[18] however their measurements of the dielectric function on well oxygenated samples only exhibited anomalies at 90 and 170 K, which were of resonant type, i.e., connected to displacive phase transitions.[7] As far as we know, also in O-deficient samples no conclusive evidence of order-disorder ferroelectric transitions is reported, although the dielectric constant is reported to have some anomalies below room temperature,[28] and to have a magnitude typical of ferroelectric materials in the tetragonal insulating state.[29]

We propose that one or more among the *PT*1-*PT*3 transitions are due to some ferroelectric [Fig. 7(c)] or antiferroelectric [Fig. 7(d)] ordering of the O atoms in the zigzag chains. In particular, we note that a transition from ferroelectric to antiferroelectric ordering, i.e., from domains of segments of type 2 to domains of segments of type 1, would imply the maximum possible change in the anelastic strain and therefore the larger effects on the elastic energy dissipation and modulus. At present, however, it is impossible to establish a precise connection between $PT1$-$PT3$ and the possible type of ordering of the O atoms among the off-center positions $(\pm\delta_x,\frac{1}{2},0)$ and perhaps also $(0,\frac{1}{2},\pm\delta_z)$.

Some considerations can be made about the consistency of the proposed model with the observed phenomenology. The intensity of the $PT1$-$PT3$ transition is expected to depend on two factors. On the one hand, one expects a weakening of the effects when lowering the O content, and therefore the amount of the phase undergoing the transition, below a certain value. On the other hand, the phase transformations should be driven especially by the electric interaction, rather than by the weaker elastic one, and such electric interaction is strongly screened by the conducting CuO_2 planes. Consequently, the transitions may be sharper when the material is less oxygenated and therefore less electrically screened. At present one cannot draw any definite conclusion from the dependence of the intensity of $PT1$-$PT3$ on x, because it is not known whether the corresponding transformations occur in the chains of the ortho-I or of the ortho-II phase, or even in chain fragments of a tetragonal phase; moreover, the phase diagram of $YBa_2Cu_3O_{6+x}$ is not known. However, we note that the occurrence of sharper transitions in samples with intermediate O content is in qualitative agreement with the above considerations.

Another point is whether it is still possible to interpret the relaxation processes $P3$ and $P4$, occurring in a presumably ordered state of the chains, in terms of jumps of the oxygens. Actually, the contradiction is only apparent, because the fact that an ordered state is thermodynamically more favorable does not imply a static order, i.e., the oxygens will continue to jump between the off-center positions, simply with a lower hopping rate, and in such a way that ordered domains exist.[30] The simplest model describing the correlated hopping of the O atoms between the off-center positions in the chains is the Ising model in the mean-field approximation. The relaxation time associated with the dynamical susceptibility can be calculated and results to be finite also below the critical temperature, although a critical slowing down occurs on approaching it.[27]

We conclude that $P4$ (and/or $P3$) can still be interpreted as due to the relaxation of the zigzag chains (or of the ordered domains in these chains) as in Ref. 13, apart from a correction to the expression of the relaxation time due the interactions. We also note that $P4$ is much broader than a single Debye relaxation peak, and this is expected for jumps of correlated atoms, with the interactions varying from place to place, according to the local microstructure.

Finally, we note that, on lowering the O concentration, $P4$ disappears already at $x \sim 0.5$, when $PT1-PT3$ are still clearly visible. This can be explained by the reduced screening of the electric interactions by the less conducting CuO_2 planes, which causes a stronger correlation among the oxygen ions and therefore a slower relaxation rate. Accordingly, peak $P4$ should shift to higher temperature and smear out, before disappearing. Indeed, a trace of a thermally activated relaxation process sometimes is visible around 120–140 K in samples where $P4$ is no more clearly detectable. This is particularly evident in Fig. 8, showing the measurement on cooling of a sample with $x = 0.2$; in the subsequent heating (not shown) $PT1$ and $PT2$ appear.

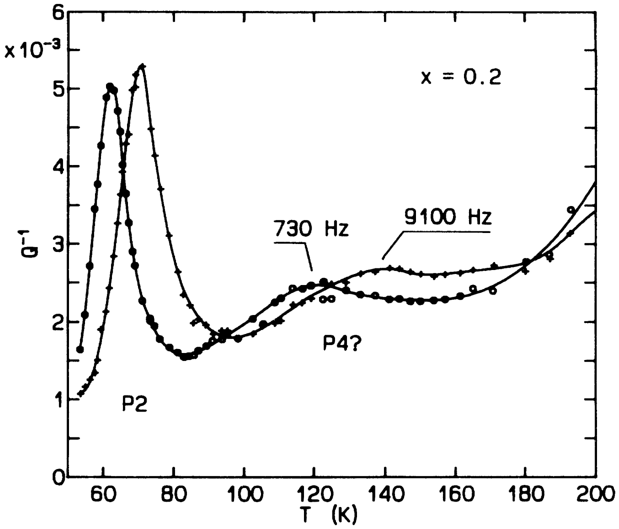

FIG. 8. Elastic energy dissipation measurement (on cooling) where peaks $P3$ and $P4$ are replaced by $P2$. A thermally activated process is well visible around 130 K, which could be $P4$ shifted to higher temperature by the interaction among the electric dipoles associated with the oxygens in the chains.

CONCLUSIONS

A considerable number of phase transformations has been revealed in $YBa_2Cu_3O_{6+x}$ below room temperature, mainly by anomalies in the elastic and dielectric properties. The transformations should be rather subtle and possible involving small domains, so that it is not yet possible to detect the involved atomic displacements by diffraction technique. In the present paper we discussed three phase transformations, $PT1$, $PT2$, and $PT3$ which appear around 120, 150, and 170 K in the elastic energy dissipation and modulus when heating after aging below 100 K. Whilst $PT3$ may correspond to a ferroelectric displacive transition appearing in the dielectric function,[7] $PT1$ and $PT2$ are only observed by measuring the elastic properties[8–11] and possibly the cell dimensions by x-ray diffraction.[8,12]

It is proposed that $PT1$ and/or $PT2$ are due to the ordering of the O atoms among the off-center positions in the Cu-O zigzag chains. Since an electric dipole is associated with O^{2-} ions in such off-center positions, ferroelectric (oxygens on the same side of the chain) and antiferroelectric (oxygen on opposite sides in zigzag fashion) domains should also form. Therefore, the present model could be conveniently tested by dielectric measurements, especially at intermediate values of the O concentration, when the screening of the conducting CuO_2 planes is less effective. The proposed interpretation correlates well with the overall phenomenology, including an anelastic relaxation process previously interpreted in terms of the nearly uncorrelated jumps of such oxygens.[13]

Note added After submitting this paper, we learned that Ting *et al.*,[31] explain a phase transformation observed by ultrasonic measurements at 260 K in $YBa_2Cu_4O_8$ and that around 240 K in $YBa_2Cu_3O_{6+x}$ as due to ordering of the zigzag Cu-O chains from a paraelectric to an antiferroelectric state. We agree that also the 240-K transformation in $YBa_2Cu_3O_{6+x}$ could be due to antiferroelectric or ferroelectric ordering of O, taking however into account that also other off-center positions are possible. Indeed, besides those of the O(1) atoms along the *a* and *c* axis, it has also been proposed that the positions of the apical O(4) oxygens are split in the *c* direction.[32] In order to assign a precise mechanism to these phase transformations there is need of measurements with different techniques (e.g., dielectric, electron microscopy).

Evidence of piezoelectric effect along the *c* axis has been reported by Mihailovic and Heeger,[33] who also observed spontaneous polarization.[34]

Also dilatometric measurements have been reported, which correlate well with the present results: You *et al.*[35] found on heating anomalies in the temperature range of the presently discussed phase transformations. Lang *et al.*[36] reported long-time drifts of the sample length between ~30 and ~60 K which were observed only during the first heating and reappeared after the sample was heated above ~110 K. The authors attributed such effects to short-range ordering below 110 K of oxygen among double well potentials.

ACKNOWLEDGMENT

This work was supported by the National Research Council of Italy under the Progetto Finalizzato "Superconductive and Cryogenic Technologies."

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