PHYSICAL REVIEW B VOLUME 54, NUMBER 21 1 DECEMBER 1996-I

Strong dependence on doping of a low-activation-energy relaxation process in $YBa_2Cu_3O_{6+x}$: Possible polaron relaxation

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(Received 15 April 1996)

The elastic energy loss of $YBa_2Cu_3O_{6+x}$ is measured below room temperature with x close to the maximum stoichiometry, where three low-activation-energy peaks are present. It is found that the intensity of the process with the lowest activation energy, $E\sim0.076$ eV decreases very steeply when x is lowered just below its maximum value; it becomes undetectable when the sample is still in the $T_c=90$ K plateau and all the other peaks are nearly unaffected. The possible mechanisms for this process are discussed, mainly in terms of hopping of polarons or off-center atoms. The characteristics that these defects should possess in order to produce anelastic relaxation are specified. The most natural way to interpret the peak is the assumption of the formation and reorientation of bipolarons among orbitals which are occupied by holes only at the highest O stoichiometries; according to Tolentino *et al.* [Physica C **192**, 115 (1992)], such holes could reside in the p_z orbitals of the apical O atoms. [S0163-1829(96)03545-X]

I. INTRODUCTION

The Y-based oxide superconductors with both 123 and 214 structure present several anelastic relaxation (AR) processes with activation energies below 0.2 eV,[1–6] but up to now none of them has been ascribed to a mechanism with certainty. The proposed mechanisms involve off-center atoms,[1,3,6] electrons or holes, i.e., polarons,[2–6] twin boundaries,[7] and dislocations.[3]

These relaxation processes are systematically observed by various laboratories on samples prepared under different conditions. Therefore, they must be due to some defect which is detectable also by other types of experimental techniques, like x-ray and neutron diffraction for off-center atoms, or various spectroscopies, NMR and NQR for polarons. This circumstance has been verified in only one case: an elastic energy-loss peak in semiconducting $YBa_2Cu_3O_{6+x}$ ($x<0.3$) with an activation energy of 0.1 eV,[8] also causes a peak in the NQR rate.[9] It is not yet established whether the effect is due to the hopping of isolated O atoms in the CuO_x plane,[8] or to hopping of small polarons.[9] In the first hypothesis there is an excellent agreement between the concentration of isolated hopping O atoms estimated by the intensities of both the AR and NQR processes (10^{-6}–10^{-5} per formula unit);[8,9] polaron hopping is also possible, but in this case the polaron concentration and local distortion are not determined.

In another case, an elastic energy-loss peak in $YBa_2Cu_3O_{6+x}$, here labeled $P4$, has been tentatively associated with the hopping of O between the off-center positions in the zig-zag Cu-O chains in $YBa_2Cu_3O_{6+x}$, which have been revealed by x-ray and neutron diffraction.[1] On the other hand, a similar AR peak is observed also in $YBa_2Cu_4O_8$,[2] where it is not proved that the Cu-O chains have a zig-zag configuration. For the sake of completeness, we mention that the same mechanism has also been suggested for an AR process around 220 K, which is observed in both $YBa_2Cu_3O_{6+x}$ and $YBa_2Cu_4O_8$.[10]

In order to find out an indication of the nature of these effects in $YBa_2Cu_3O_{6+x}$, AR measurements have been made on samples which were outgassed from O,[2–4] or with Y partially substituted by Pr (Ref. 4) or Ca,[5,6] to change the concentration of free holes. All of these peaks are more or less affected by the above substitutions, and this is considered as an indication that the holes are responsible for them.

In the present paper we will focus on the peak with the lowest activation energy in $YBa_2Cu_3O_{6+x}$, here labeled $P1$, and we will show that it is strongly dependent on the O concentration in the restricted range $0.85<x<1$, disappearing below it. This also can be interpreted as due to polarons existing only above a certain doping level, using existing models of the holes configurations in $YBa_2Cu_3O_{6+x}$.

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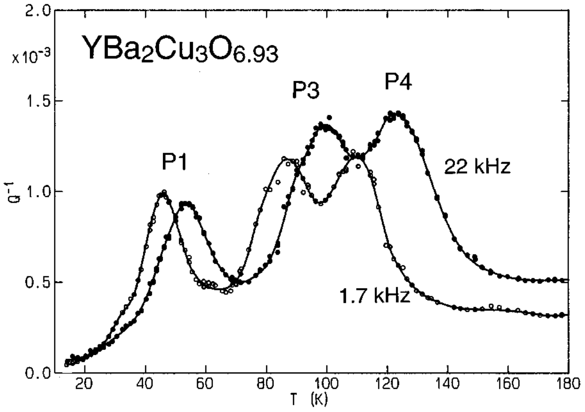

FIG. 1. Elastic energy loss of $YBa_2Cu_3O_{6.93}$ measured on both the first (1.7 kHz) and fifth (22 kHz) flexural vibration modes.

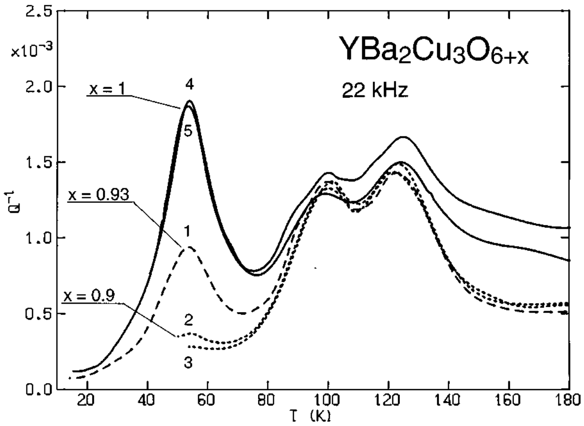

FIG. 2. Elastic energy loss (fifth flexural mode) of a same sample of $YBa_2Cu_3O_{6+x}$ at three different O contents.

II. EXPERIMENTAL AND RESULTS

The sample was a sintered bar of $YBa_2Cu_3O_{6+x}$ with dimensions 43×4.3×0.9 mm^3. The starting material did not contain carbonates; it was calcined in air at 1233 K for 6 h, sintered in fluent oxygen at 1253 K for 22 h and oxygenation was completed at 773 K for a few hours. The initial oxygen content was estimated as $x=0.93\pm0.03$, and the resistivity displayed the superconducting transition at 90.3 K with a width of 1.3 K and zero resistance at 88 K. We will refer to this state of the sample as to the $x=0.93$ state.

Figure 1 shows the $Q^{-1}(T)$ measured on cooling exciting the first (1.7 kHz) and fifth (22 kHz) flexural modes. The measurement was made six years after the sample preparation and oxygenation ($x=0.93$). This long ageing at room temperature in dry air did not affect the sample, since the $Q^{-1}(T)$ curves of a specimen from the same batch measured just after preparation are closely similar to those in Fig. 1. These are also the typical curves measured by us in several samples and by many other groups. The three peaks below 180 K are labeled $P1$, $P3$, and $P4$, and are all thermally activated, as deduced from their temperature shift at the two vibration frequencies; their activation energies are 0.076, 0.16, and 0.19 eV, respectively.

In what follows we will describe the effect of changing the O content, remaining within the $T_c=90$ K plateau. Figure 2 shows the $Q^{-1}(T)$ curves with the sample in three different conditions; the resonant vibration frequencies did not change by more than 10% between the first and the last run. It is apparent that the intensity of $P1$ changes drastically by changing little the O content, while those of the other two peaks remain nearly unaffected. Curve 1, with $x=0.93$, corresponds to Fig. 1.

The sample was then aged for 20 h in a vacuum better than 10^{-5} mbar at 470 K and cooled to room temperature at 0.85 K/min. In order to estimate the possible O loss during vacuum annealing, we measured again the electrical resistance, which showed $T_c=92.0$ K and zero resistance at 89.6 K. Comparing this value of T_c with the results of Ref. 11 we estimate $x>0.85$. Similar vacuum annealings at 590 K for 30 h on sintered pellets with $x=0.94$ have been reported to yield $x=0.90$,[12] besides rising T_c and narrowing the superconducting transition as in the present case. This is possible if the sample was originally in an overdoped state. Since our annealing was milder, we conclude that when curve 2 of Fig. 2 was measured, the O content of the sample was $x=0.90\pm0.05$; we will refer to this state as the $x=0.9$ state. After this slight reduction of the O content, the $Q^{-1}(T)$ curve remained unaffected, except for peak $P1$ which was reduced by 3–4 times (curve 2). The intensity of $P1$ was further reduced in subsequent measurements during the following 15 days, possibly due to some reordering of the O vacancies (curve 3 being the last one).

The sample was again oxygenated in order to achieve a concentration of O as close as possible to 7 ($x=1$ state). It was heated up to 600 °C in a quartz tube connected with a UHV system; at this temperature a static atmosphere of 1250 mbar O_2 was established and the specimen was slowly cooled to room temperature, where the O_2 pressure was reduced to 740 mbar. The cooling rate was 0.2 K/min except between 490 and 300 °C, where it was reduced to 0.1 K/min in order to maximize the O uptake. The oxygenation treatment raised the whole $Q^{-1}(T)$ (curve 4), but the greatest effect was on $P1$, which was enhanced by about two times with respect to the height in the original state ($x=0.93$), and more than eight times with respect to the last measurement ($x=0.9$). The measurement was reproduced during subsequent cooling runs (curve 5).

The reproducibility of the phenomenology was checked again (results not shown) with the absence of $P1$ in the partially outgassed state ($x\sim0.87$) and its recovery in the fully oxygenated state ($x\sim1$). The sample was first outgassed in the UHV system and a known amount of O_2 was admitted, in order to obtain an equilibrium pressure of 9.6 torr at 460 °C. According to the pxT diagram of Ref. 13, the equilibrium value of x in such conditions is $x=0.85$; the value estimated by the amount of gas absorbed was 0.89 ± 0.04. In this state, which we call "$x\sim0.87$," peak $P1$ was absent, and its intensity was again recovered to 90% of its maximum value after an additional oxygenation to $x\sim1$ in 1300 mbar O_2 with cooling rates below 500 °C about twice higher than during the preceding full oxygenation treatment. The fact that $P1$ was not fully recovered is consistent with the faster oxygenation, which yields a slightly lower oxygen stoichiometry.

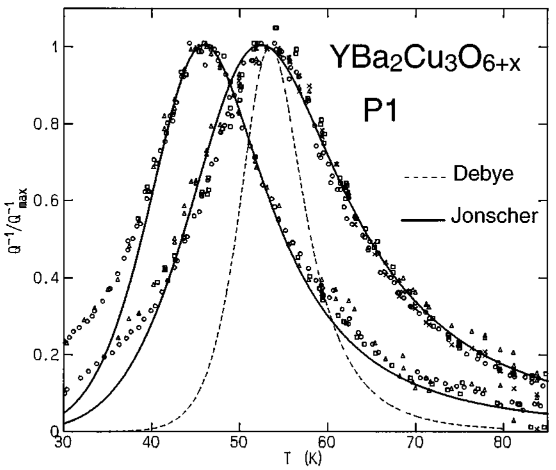

FIG. 3. Normalized elastic energy loss at 1.7 and 22 kHz due to $P1$, after subtraction of the background and the other peaks $P3$ and $P4$. Different symbols refer to different curves of Fig. 2: curve 1 with $x=0.93$ (triangles), curve 4 (squares), and curve 5 (circles) with $x=1$. The crosses are the difference between curve 4 and curve 2 of Fig. 2, without any background subtraction. The dotted line is the theoretical curve assuming single Debye relaxation, while the continuous lines are obtained assuming the relaxation function proposed by Jonscher, with a restricted number of parameters.

III. DISCUSSION

The main feature of $P1$ is the strong reduction of its intensity on lowering the O content in the restricted range $0.85<x<1$, where most of the other physical properties are nearly constant. Other features of $P1$ are its stability over long times (at least six years), and the reproducible dependence of its intensity on x, which exclude that it is due to some impurity phase at the grain boundaries. Finally, the temperature and shape of $P1$ are little or not affected by the oxygen stoichiometry, as demonstrated in Fig. 3. In this figure the measurements in the $x=0.93$ and $x=1$ state are reported after subtraction of the background and of the contributions of the other peaks and after normalization of the intensity. The normalized points fall on the same curve with excellent approximation, except for the lowest temperatures, where the effect of the background subtraction is stronger (since the actual background is unknown, a linear function of temperature was chosen between 0 and 300 K). In order to check the validity of the subtraction of the other contributions, we also reported the difference between the experimental curves 4 and 2 of Fig. 2; the two measurements differ only in the height of $P1$. After normalization, also these data fall on the same curve, confirming the consistency of the procedure.

An analysis of the shape of $P1$ shows that it is markedly broader than a Debye relaxation process. The elastic energy loss of a process with a single relaxation time τ is[14]

$$Q^{-1}=\Delta\,\frac{1}{\omega\tau+(\omega\tau)^{-1}}, \tag{1}$$

where $\omega=2\pi f$ is the angular vibration frequency of the sample; $Q^{-1}(T)$ is maximum at $\omega\tau=1$ (neglecting the temperature dependence of the relaxation strength Δ). The mean relaxation time derived from the above condition at the two vibration frequencies in Fig. 3 may be fitted with the usual Arrhenius law $\tau=\tau_0 e^{-E/kT}$, with $\tau_0=5\times10^{-13}$ s and $E/k=880$ K. However, substituting this $\tau(T)$ in the expression of $Q^{-1}(T)$, one obtains a peak narrower than the experimental one, indicating that there is either a distribution of relaxation times, or a non-Debye relaxation. The single Debye process is shown as a dashed line in Fig. 3. The effective activation energy necessary to obtain the correct peak width is $E_W/k\sim350$ K, and the ratio $\alpha^{-1}=E/E_W\sim2.5$ is a measure of the width of the peak. Values of α close to 1 indicate processes with only one relaxation time, and can be found for noninteracting and very diluted point defects, the typical example being the hopping of interstital O, N, and C in bcc metals (Snoek effect).[14] In $YBa_2Cu_3O_{6+x}$, the only peak which approximates a Debye process with $\alpha^{-1}\sim1.25$ is the one appearing at $x<0.3$ with an activation energy of 0.1 eV,[8] which we attribute to the hopping of isolated O atoms in the CuO_x plane (see also the introduction).

A. Geometrical defects

The present value of the peak width with respect to a Debye process, $\alpha^{-1}\sim2.5$, is characteristic of strongly interacting or disordered systems or of the relaxation of geometrical defects (dislocations, domain boundaries, . . .) whose microscopic configurations are distributed according to a broad spectrum. On the other hand, the reproducibility of the peak shape is against an interpretation in terms of geometrical defects, which generally produce peaks whose temperature and shape change with the sample conditions. Moreover, it is doubtful whether the expected low density and slow mobility of dislocations can cause a peak with that intensity and at such a low temperature. Indeed, $P1$ may recall some dissipation peaks due to dislocation relaxation in deformed metals, but the density of dislocations in sintered $YBa_2Cu_3O_{6+x}$ samples ($\leqslant10^7$ cm^{-2}),[15] is some orders of magnitude lower than in a deformed metal (10^{10}–10^{12} cm^{-2}); in addition, the dislocation mobility is much lower than for a metal, as deduced from plasticity studies at high temperature.[16]

The twin boundaries between the two possible orientations of the Cu-O chains in the CuO_x planes are certainly much more mobile and abundant than dislocations, but again we would not expect a stable peak shape, and it would be difficult to explain its disappearance at $x<0.8$, when twin boundaries are still present. We think that twin boundaries would rather produce the dissipation maximum often observed near 220 K, which is little reproducible and accompanied by a hysteresis between heating and cooling of the elastic constants.[10,17]

B. Relaxation intensity and defect shape factor

The other types of defects which can cause anelastic relaxation with an activation energy as low as that of $P1$ are polarons and off-center atoms. Before discussing the two possibilities, we first point out what characteristics should possess a point defect, in order to cause the observed anelastic relaxation. The sample is polycrystalline and therefore nothing can be said on the symmetry of the point defect, except that its jumps must be accompanied by a reorientation or change of the local distortion (elastic dipole tensor λ_{ij}). In fact, if a jump causes a change $\Delta\lambda_{ij}$ of the ijth component of the local distortion, the ijth contribution to the relaxation strength in Eq. (1) is[14] $\Delta \sim (c/T)(\Delta\lambda_{ij})^2$, where c is the concentration of hopping atoms; $\Delta\lambda$ is also called shape factor. The distortion around the defect can be visualized as a strain ellipsoid with the principal axes given by the coordinate system where the λ_{ij} tensor is diagonal.[14] The hopping of the defect causes a reorientation of the ellipsoid, when the possible defect configurations are equivalent but with different possible orientations. Instead, hopping among nonequivalent configurations also causes a change of the ellipsoid. This case involves also a change of the defect energy, and the relaxation strength becomes[18]

$$\Delta(T) \sim \frac{c_1 c_2}{c}\frac{1}{T}(\Delta\lambda)^2 \sim c\,\frac{1}{T\cosh^2(\Delta E/kT)}(\Delta\lambda)^2, \quad (2)$$

where c_1 and c_2 are the populations of the defect in the configurations 1 and 2, which differ in energy by ΔE. The change in defect energy causes a reduction in the relaxation strength and $\Delta\,(T)$ becomes a strongly increasing function of T for $kT < \Delta E$. In the present experiments, the ratio of the peak values of $P1$ at the two vibration frequencies is between 1 and the reciprocal of the ratio of the peak temperatures, and therefore $\Delta E/k$ must be of the order of 50 K or less. This means that $P1$ is likely caused by the reorientation of a point defect among nearly equivalent configurations. In what follows we will discuss $P1$ in terms of hopping of atoms among off-center positions and in terms of polaron hopping.

C. Atoms in off-center positions

The splitting of an atomic site in several off-center positions is common in perovskite-related materials, and the activation energy for the atomic hopping among close positions can be very low. In $YBa_2Cu_3O_{6+x}$ the O atoms in the Cu-O chains occupy slightly off-center positions in the ab plane, as deduced from neutron[19] and x-ray diffraction[20] experiments, and it is debated whether also the apical oxygens feel a double-well potential in the c-axis direction. The short jumps of the O atoms between the off-center positions have been proposed to cause the relaxation peak $P4$.[1] Note that hopping of an atom within a pair of off-center positions related to each other by inversion symmetry does not cause anelastic relaxation, because the strain tensor is centrosymmetric and does not change after an inversion (the strain ellipsoid remains unchanged after a reorientation by 180°). For this reason, the relaxation unit proposed for $P4$ (Ref. 1) was not a single O in the zig-zag chain, but a pair of adjacent oxygens bridged by a Cu atom. The elastic dipole of a pair changes when its configuration passes from both oxygens on the same side with respect to the chain to the configuration with the oxygens on both sides. The atomic rearrangement and the consequent change of the local distortion is small, but is compensated by the high concentration of relaxing units. This case corresponds to a change of the shape of the strain ellipsoid, rather than to its reorientation. The gradual disappearance of $P4$ on lowering the O content can be explained by the gradual shortening and disappearance of the Cu-O chains, although nothing quantitative can be stated at present. On the contrary, the same mechanism cannot be invoked for $P1$, due to its fast disappearance when lowering x just below 1.

Other off-center atomic positions can be supposed, although they have never been seen by diffraction methods, possibly in correspondence to lattice imperfections like substitutional atoms or vacancies or interstitial impurities. In fact, a small concentration of off-center positions associated with imperfections could be difficult to reveal by diffraction experiments. Again, one has to explain the strong dependence of the relaxation intensity on x; a possibility would be an unfavorable configuration of an oxygen near an imperfection, which is occupied only at the highest values of x, when all the other positions are already occupied. If the concentration of these unknown off-center configurations is so small that they are not observed by diffraction, than the jump of each off-center atom should produce a sizeable reorientation of the elastic dipole; for example, hopping among four positions in square coordination, or six positions in octahedral coordination near an imperfection.

D. Hopping of polarons

Another plausible mechanism for $P1$ is the hopping of a polaron. Relaxation of electronic nature has been suggested for the low-activation-energy processes in $YBa_2Cu_3O_{6+x}$,[2–6] and both the very low-activation energy of $P1$ and its strong dependence on doping through x and through the ordering of the O vacancies are indicative of polaronic relaxation.

The elastic dipole associated with the polaron should be nonisotropic and should change its orientation after a jump of the polaron, as noted above for the case of an off-center atom. Therefore, a hole residing on O atoms of the CuO_2 planes could give rise to anelastic relaxation, because when they jump from an O to another, the direction of the nearest neighboring Cu atoms reorients itself by 90° together with the local distortion. On the contrary, a hole residing on an orbital of the Cu atom and possessing the whole symmetry of that atomic site, would just translate its local distortion during a jump, without affecting the overall strain of the crystal (the elastic dipole would not change). Such a hole could produce anelastic relaxation only if trapped by an imperfection, or if paired to another hole to form a bipolaron; in this case the local symmetry is lowered to that of the pair, and reorients itself during a jump. The case of a polaron which relaxes transitions between two nonequivalent states can be considered only if such states differ in energy by no more than 50 K as discussed in Sec. III B. Of course, it is possible that the relaxation between strain-split equivalent states occurs through an activated mobile state; in this case the activation energy is the energy necessary for reaching the mobile state.

E. Possible polaron configuration

To our knowledge, the best model for the holes configuration in $YBa_2Cu_3O_{6+x}$ is that of Tolentino *et al.*,[21] based on spectroscopic observations on the valence of Cu and on the character of the holes. According to their model, starting from $YBa_2Cu_3O_6$ and adding O^{2-}, the holes are first localized in the Cu-O chains and start being pushed by the electrostatic repulsion to the CuO_2 planes for $x > 0.25$, where they are localized on the $p_{x,y}$ orbitals of the O(2) and O(3) atoms. At $x > 0.8$ they observed also holes of character p_z, possibly localized on the apical O(4).

According to this model, the p_z holes could be responsible for $P1$, but not through the hopping of single holes. In fact, the p_z orbitals are all equivalent and the simple translation of the strain associated with the hole does not produce anelastic relaxation. Instead, the reorientation of a close pair of holes (a bipolaron) could well explain a process like $P1$. Moreover, it would also explain the steep increase of $P1$ with increasing x, because its intensity would be roughly proportional to the square of the concentration of the p_z holes.

The polaron hopping rate ν (corresponding to the reciprocal correlation time of NQR and NMR experiments) should also be consistent with the relaxation rate of $P1$ deduced from the condition $\omega\tau = 1$ at the peak maximum at the two different vibration frequencies, i.e, $\nu \sim \tau^{-1} \sim 5 \times 10^{-13} \exp(-880/T)\ \mathrm{s}^{-1}$; the exact relation between ν and τ^{-1} depends on the number and geometry of the possible polaron configurations. It is clear that the hopping rate involved in $P1$ is much slower than the mobility of the holes involved in the electric conduction ($P1$ is observed while the sample is superconducting). Indeed, the p_z holes on the apical O are expected to be far less mobile than the holes in the planes, and the reorientation rate of a bipolaron may be much slower than the mobility of the individual polarons. It is also possible that the bipolaron is formed in correspondence to an imperfection, which tends to localize it and slow its mobility.

It is worth noting that recently Bidault *et al.*[22] found a dielectric relaxation in several perovskites, which has the same activation energy as $P1$, but a narrower distribution of relaxation times. The authors attribute such a relaxation to polarons localized in nonidentified residual point defects, which are present in all their samples.

F. Effect of cation substitution on *P*1

Peak $P1$ has also been observed by Gazda *et al.*[4] in $Y_{1-y}Pr_yBa_2Cu_3O_{\sim 7}$, and it is gradually suppressed and replaced by another process with an even lower activation energy, when proceeding with Pr substitution. The same authors[3] also observed the suppression of $P1$ in Fe-doped samples with a Fe concentration as low as 1.75%. To our knowledge there is no consensus on the effect of Fe doping on the holes in $YBa_2Cu_3O_{6+x}$, while it has been proposed that Pr localizes them.[23] Therefore, we assume that these results are not in contrast with the assumption that the intensity of $P1$ is a strongly increasing function of the hole concentration, above a certain threshold which is close to the maximum value. In view of the strong dependence of the intensity of $P1$ on the O content, one should also consider the possible effect of the substitution on the O stoichiometry.

G. Hopping rate: disordered or correlated system

As noted at the beginning of this section, peak $P1$ is about 2.5 times broader than a single Debye peak. This broadening may result both from a static distribution of E and/or of τ_0, and from a dynamic interaction among the relaxing entities, but the distinction between the two contributions is not obvious.

In a ceramic sample of $YBa_2Cu_3O_{6+x}$, there are several causes of static disorder, like the O vacancies, the twin boundaries, and the grain boundaries. In the assumption of static disorder, the broadening of $P1$ can be reproduced by assuming a Gaussian distribution of activation energies with a width of the order of 10% of the mean activation energy, $E \sim 880$ K. Such a dispersion of activation energies seems justifiable by the highly disordered lattice of $YBa_2Cu_3O_{6+x}$, and can be compared with the case of the hopping of hydrogen trapped by substitutional Ti in Nb.[24] In that case the disorder arises from a few at. % of substitutional Ti and the experimental dissipation peaks require distributions of the activation energies whose widths are even 30% of their mean value.

In the assumption of dynamic interaction between the relaxing entities, the peak broadening cannot be treated in a standard way. There is a vast literature on non-Debye dielectric and mechanical relaxation in disordered and correlated systems like glasses or ionic conductors, but a coherent model has not been formulated yet.[25] Jonscher proposed the phenomenological relaxation function[26]

$$Q^{-1} = \Delta \frac{1}{(\omega\tau_1)^{-m} + (\omega\tau_2)^{1-n}}, \tag{3}$$

where $\tau_1(T)$ and $\tau_2(T)$ are two relaxation times, possibly following the Arrhenius law, which describe the relaxation of the system at short and long times. Expression (3) can well interpolate several relaxation phenomena in complex and correlated systems,[26,27] but it has not been derived in a rigorous way. It becomes the Debye relaxation function when $\tau_1 = \tau_2$, $m = 1$ and $n = 0$, and the Fuoss-Kirkwood expression for $m = 1 - n = \alpha$.

We attempted a fit of $P1$ with Eq. (3) with $\tau_1 = \tau_2 = \tau_0 \exp(E/kT)$, and obtained $E = 945$ K, $m = 0.41$, and $n = 0.67$. The resulting theoretical curves are the solid lines in Fig. 3. The satisfactory fit indicates that $P1$ can be treated like other relaxation processes in strongly correlated or disordered systems (e.g., the ionic conductor β-alumina[27]), but it is difficult to assign a precise physical meaning to the fit.

On the other hand, when the intensities of these processes are varied, generally also the shape and temperature of their relaxation functions change. This has also been observed by NQR for the hole diffusion in the La oxides[28] and in Li-doped CuO;[29] in that case the hole mobility is thermally activated through a gap between a localized and a mobile state of the hole, and the gap is observed to be a function of the hole concentration. Instead, the shape of $P1$ does not change much with x, but this can be explained by the fact that the interactions producing the peak broadening, whether static or dynamic, do not occur between the relaxing polarons, because their concentration is too low for a reciprocal influence among themselves. Each relaxing polaron interacts with the other mobile charge carriers and the disordered environment, which are nearly constant in the range $0.9 < x < 1$.

IV. CONCLUSIONS

We studied the dependence on the O stoichiometry of the anelastic relaxation process with the lowest activation energy in $YBa_2Cu_3O_{6+x}$, $E/k \sim 880$ K. The main characteristics of this process are (i) its intensity is maximum at the maximum

O stoichiometry, and steeply decreases below it; the dissipation peak cannot be distinguished from the background for $x<0.85$; (ii) the process is about 2.5 times broader than a Debye relaxation, and can be fitted by the Jonscher relaxation function usually adopted for strongly disordered or correlated systems; (iii) the peak shape is nearly independent of the intensity, contrary to the usual disordered or correlated systems.

Possible mechanisms for $P1$ have been discussed: geometrical defects, off-center atoms and polarons. It is concluded that the last two types of defects are likely responsible for $P1$. In the case of hopping of an atom among off-center positions, one should look for an unfavorable configuration of an oxygen near an imperfection, which is occupied only at the highest values of x. In the case of polaron hopping, one should look for bipolaron reorientation, or for orbitals with at least two different orientations, so that the single hole hopping causes a reorientation of the local strain. It is proposed that $P1$ is due to the formation of bipolarons in the p_z orbitals of the apical O atoms, where the holes are observed only at the highest O stoichiometries; this would explain in a natural way the steep increase of the intensity of $P1$ in the restricted range $0.85<x<1$.

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