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TITLE: MECHANICAL AFTER-EFFECT STUDIES OF OXYGEN RELAXATION IN $YBa_2Cu_3O_{7-\delta}$

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MECHANICAL AFTER-EFFECT STUDIES OF OXYGEN RELAXATION IN $YBa_2Cu_3O_{7-\delta}$

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ABSTRACT

$YBa_2Cu_3O_{7-\delta}$ has an anelastic relaxation involving motion of an oxygen atom or defect. This relaxation has been studied with good agreement by more than seven investigating teams over the temperature range from 200 to 550°C using internal friction techniques. We have extended measurements of this relaxation to a new regime of temperature and relaxation time using the mechanical after-effect method. Our results cover an additional three orders of magnitude in relaxation time over the temperature range from 50 to 110°C. The Arrhenius plot, when combined with internal friction results, now covers eleven orders of magnitude in relaxation time. The fit gives an activation energy, $Q=1.12$ (±0.015) eV and a pre-exponential, $\tau_0= 1.9\text{x}10^{-13}$ s.

The isothermal mechanical relaxation curves we measured always spanned longer times than predicted for a simple exponential relaxation. This indicates that the process is controlled by a relatively wide spectrum of relaxation times. We have calculated best approximations of this spectrum by deconvoluting the mechanical after-effect curves. The resulting distribution is symmetrical in logarithm of the relaxation time with a width at half-height which is a factor of 20 in relaxation time. The significance of these findings is discussed in terms of our understanding of oxygen mobility in $YBa_2Cu_3O_{7-\delta}$.

1. INTRODUCTION

It is desirable to better understand the atomic mobility of oxygen in $YBa_2Cu_3O_{7-\delta}$ because the oxygen stoichiometry and thus the superconducting properties are determined during fabrication by controlling diffusion of oxygen into the bulk. Anelastic relaxation studies, especially those which involve jumping of atoms between sites, have in the past been important to our understanding of atomic mobility in many metals and ceramics. Our focus for this paper is the further investigation of oxygen mobility in $YBa_2Cu_3O_{7-\delta}$ through anelastic studies using the mechanical (i.e., elastic) after-effect (MAE) method. This technique complements internal friction (IF) studies by measuring in a temperature regime with longer relaxation times.

2. PRIOR ANELASTIC STUDIES

An IF peak due to orientational ordering of oxygen atoms in $YBa_2Cu_3O_{7-\delta}$ was first reported by Berry [1]. This anelastic relaxation was manifested by a peak at 600 K measured at roughly 350 Hz. This relaxation was considered to be due to jumping of oxygen atoms between sites on the CuO plane. It should be noted that Berry and other investigators also observed IF peaks due to oxygen in $YBa_2Cu_3O_{7-\delta}$ at subambient temperatures. These anelastic relaxations are not considered in this paper since their low activation energies indicate that they involve jump distances for oxygen of less than an interatomic spacing.

Other researchers independently found and investigated this oxygen relaxation soon after Berry. Tallon and coworkers [2], who were first to confirm the effect, reported a peak at 800 K measured at 40 Khz. Later they investigated the same peak when they extended their measurements to frequencies of 8 and 144 Khz [3]. Subsequently, this oxygen relaxation was reported at torsional pendulum frequencies by Zhang and coworkers [4-6], Xie et al [7], and Cost and Stanley [8]. Also, Berry and coworkers [9], Bonetti et al [10], as well as Cost and Stanley [8] investigated this peak at frequencies near 1 kHz and found it to be a manifestation of the same oxygen relaxation.

The Arrhenius plot of the relaxation time for oxygen obtained by IF by all the above researchers is shown in Figure 1. The predicted temperature dependence of the relaxation time τ is

$$\tau(T) = \tau_0 \exp(-Q/kT) \qquad (1)$$

It is satisfying to see that the relaxation time for oxygen in $YBa_2Cu_3O_{7-\delta}$ shows a good linear fit to the Arrhenius relation over more than seven orders of magnitude, a strong indication that this relaxation has a single rate-controlling mechanism over the temperature range from 400 to 880 K. This fit gives an activation energy $Q=1.05$ eV and a pre-exponential factor $\tau_0=9.3\times10^{-13}$ s (ignoring the results of Bonetti et al [10]). The agreement we observe in Figure 1 is surprising since the measurements were, of course, performed on different samples prepared in different laboratories, often by different methods. It indicates that the rate of the oxygen relaxation is not highly structure sensitive, and especially that it does not depend greatly upon oxygen stoichiometry.

There is, however, a measurable effect of stoichiometry upon the relaxation time. This has been shown by Berry and coworkers [9] as a shift in peak temperature T_p with loss of oxygen. Notice the three solid circle data points in Figure 1 which are for various annealing times at 773 K. T_p of an as-prepared sample (middle point of the three) is 607 K; after degassing of oxygen by an anneal of 13 hours T_p drops to 565 K; then, a further anneal of 49 hours causes T_p to increase to 620 K. From Figure 1 we can see that this variation in T_p with oxygen loss corresponds to a deviation in the relaxation time at constant temperature of almost one decade. Interestingly, the relaxation time first decreases and then increases with loss of oxygen. Unfortunately, no systematic measurements have yet been made to show the details of how the relaxation time depends upon δ.

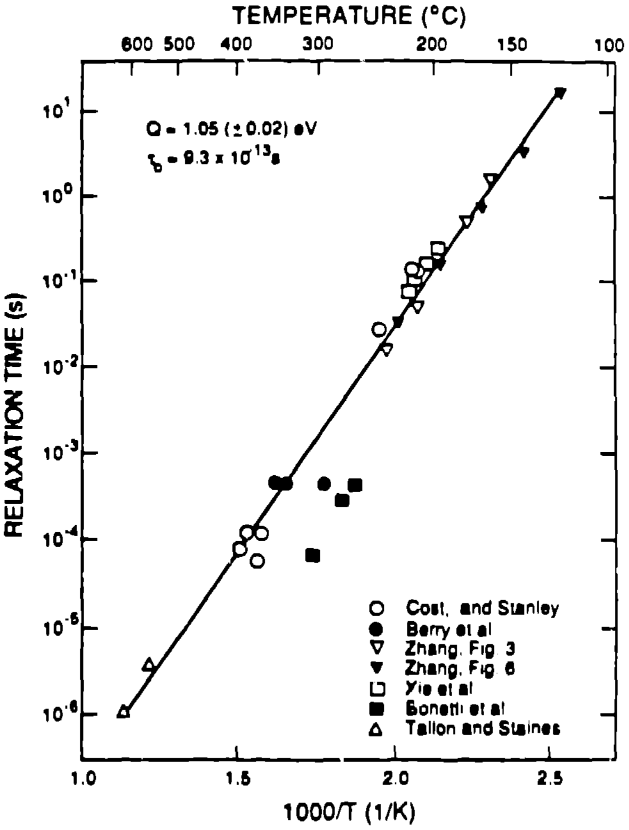

Figure 1. Arrhenius plot of relaxation time for oxygen relaxation measured by internal friction.

The only data which are not a good fit to the plot in Figure 1 are those of Bonetti and coworkers [10]. The temperature dependence of their results is consistent with that obtained by other workers; however, their relaxation time values at a given temperature appear to be too low by a factor of roughly twenty. This does not appear to be a stoichiometric effect; they measured δ of their samples to be in the range from 0.05 to 0.10 which is not significantly different from δ values reported by other researchers [8]. Thus we are not presently able to know the cause for the deviation of their results.

In all of the above IF studies it has been observed that the IF peaks are wider than predicted for a single relaxation time. This is not unexpected; it indicates that oxygen atoms involved in the relaxation are jumping from a range of local environments and thus have a spectrum of relaxation times. To know more about the relaxation of oxygen atoms, it is desirable to investigate this distribution, especially its width and shape. MAE measurements, being isothermal, are more accurately analyzed by DSA than those of IF, i.e., they do not require assumptions concerning the temperature dependence of the relaxation parameters. Also, MAE measurements supplement those by IF by extending the relaxation time measurements by several decades.

3. EXPERIMENTAL PROCEDURE

The experimental method for making MAE measurements in $YBa_2Cu_3O_{7-\delta}$ has previously been described [11]. Briefly, isothermal measurements were made of the anelastic strain in torsion as a function of time following application of a constant torsional stress at temperatures from 50°C to 110°C. All the measurements were made on two wire samples, which also were the same ones used for previous IF measurements [8]. Oxygen stoichiometries of the two samples were measured as $\delta=0.10$ and 0.17. MAE experimental results from the two samples were essentially the same.

Results from a typical MAE experiment on $YBa_2Cu_3O_{7-\delta}$ are shown in Figure 2, which is a plot of torsional strain versus time for a $YBa_2Cu_3O_{7-\delta}$ sample measured at 90.6°C. First, the stress-loading type of experiment is shown on the left side of Figure 2. Here the unstressed and fully relaxed sample (A to B) is loaded with a constant stress at $t_{\sigma>0}$ to cause instantaneous elastic strain ϵ_{el} (B to C) and subsequently anelastic strain (C to D). After holding several relaxation times the strain becomes constant giving the total anelastic strain ϵ_{an}. If the time dependence of the relaxation is governed by a single relaxation time τ, the anelastic strain is given by

$$\epsilon(t) = \epsilon_{el} + \epsilon_{an}\,[1-\exp(-t/\tau)] \tag{2}$$

with $t=0$ at the loading time, $t_{\sigma>0}$.

A typical stress unloading experiment is shown at the right side of Figure 2. It requires that previously there have been a relaxation under constant applied stress which occurred to completion. To start the relaxation the stress is then set to a new value, typically zero. Measurements are then started with $t=0$ at $t_{\sigma=0}$. As with the loading experiment, the instantaneous elastic strain (D to E) is followed by the time-dependent anelastic strain (E to F). For a single relaxation time the anelastic strain decays exponentially according to

$$\epsilon(t) = \epsilon_{an} \exp(-t/\tau). \tag{3}$$

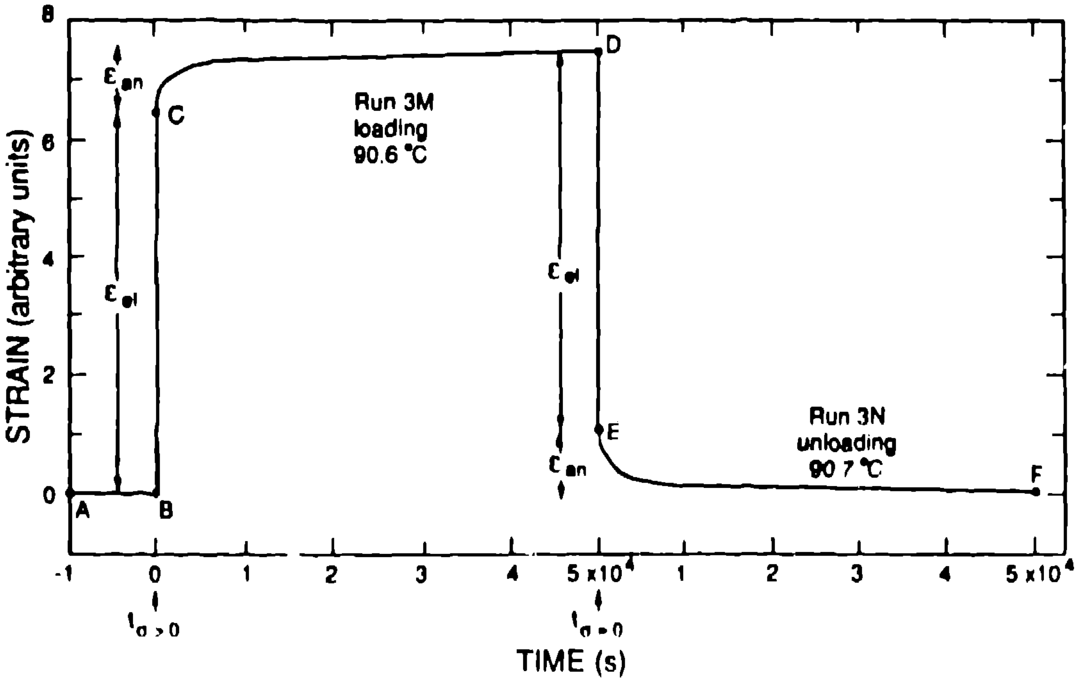

Figure 2. Mechanical after-effect measurements on $YBa_2Cu_3O_{7-\delta}$ at 90.6°C. Torsional strain is plotted versus time, first for loading (B to D), and then for unloading (D to F). The strains are fully reversible.

Since the oxygen relaxation in $YBa_2Cu_3O_{7-\delta}$ is controlled by a spectrum of relaxation times [8], the expression for strain requires integration of Equation 2 (or 3) over this spectrum. To calculate this spectrum, this integral equation must be unfolded [12].

METHOD OF ANALYSIS

The strength of the relaxation for a MAE experiment is given by $\Delta=\epsilon_{an}/\epsilon_{el}$. For the isothermal measurements at 90.6°C shown in Figure 1 we obtain $\Delta=1.1/6.4=0.172$.

For either the loading or the unloading experiment, the strain versus time curve may be analyzed to obtain an average relaxation time. For the MAE results on $YBa_2Cu_3O_{7-\delta}$ the anelastic response curves are spread out in time more than would be predicted for a single relaxation time. As has been discussed for the IF results [8], this is because a relatively wide spectrum of relaxation times controls the relaxation kinetics. The relaxation time which we report is τ_{infl}, the time at the inflection point of the anelastic strain versus logarithm of time plot. It has been shown that τ_{infl} provides an average near the center of the relaxation time spectrum [13]. Throughout this paper the symbols τ_{infl} and τ will be used interchangeably. The inflection point analysis of the results shown in Figure 2 gave values of τ of 700 s and 650 s for the loading and unloading experiments, respectively. The uncertainty in measurement of τ is estimated at 40%.

One of the most interesting and important results to be obtained by analysis of MAE curves is information about the spectrum of relaxation times which controls the relaxation. Details of this spectrum and its temperature dependence provide basic understanding of the atomic jump process. We have developed a method for analysis of exponential decay kinetics when the reaction is controlled by a continuous spectrum of relaxation times such as with MAE curves. Referred to as the Direct Spectrum Analysis (DSA) method, this technique provides a reliable approximation of the position, shape, width, and magnitude of the desired spectrum [12,14]. The DSA method deconvolutes a MAE curve by assuming that it is due to a large number of discrete relaxation times which are at logarithmically equally-spaced intervals over a range large enough to account for the relaxation. The method uses nonlinear regression to iteratively find the weighted contribution to the total process of each of the discrete relaxation times. The DSA technique has been validated on computer-generated data and shown to calculate dependable approximations of a wide variety of known input spectra [12]. It has been shown to have an accuracy for the calculated spectra which is roughly the same as the experimental error in the data.

4. RESULTS AND DISCUSSION

A. Relaxation time spectrum

The results from a loading MAE experiment at 79.8°C are shown in Figure 3a. Here fractional anelastic strain data are plotted versus time on a logarithmic scale. That the MAE curve spans a much longer time than for a single relaxation may be seen by comparison with the dashed curve which is for fractional exponential decay with a relaxation time of 5500 seconds.

The DSA results calculated for the data in Figure 3a are shown in Figure 3b. Here the spectral amplitude N(ln τ_i) for each of 33 τ_i's is plotted versus the τ_i value. Other DSA calculations done for the same data, but with the analysis parameters varied (e.g., number of τ_i) showed spectra which only differed from that in Figure 3b by a few percent. Also, DSA spectra calculated from other MAE experiments on $YBa_2Cu_3O_{7-\delta}$ were similar to the one shown.

We note that the relaxation time spectrum is quite broad, ranging from 400 s to 70,000 s at half height. Also, it is symmetrical on the log(τ_i) scale. The combination of breadth and symmetry suggests that it may be a good fit to a lognormal distribution. The tendency for relaxation time spectra to fit a lognormal distribution and the properties of such a distribution have been discussed in detail by Nowick and Berry [13]. A lognormal curve fit to the DSA spectrum is shown as the dashed curve in Figure 3b. This fit gives τ_m=5130 s for the center of the distribution and ß=3.25 for the width parameter. The inflection point analysis of these data gave τ_{infl}=3700 s, roughly 30% less than τ_m obtained by DSA. This is an intrinsic difference due to the averaging of the τ spectrum.

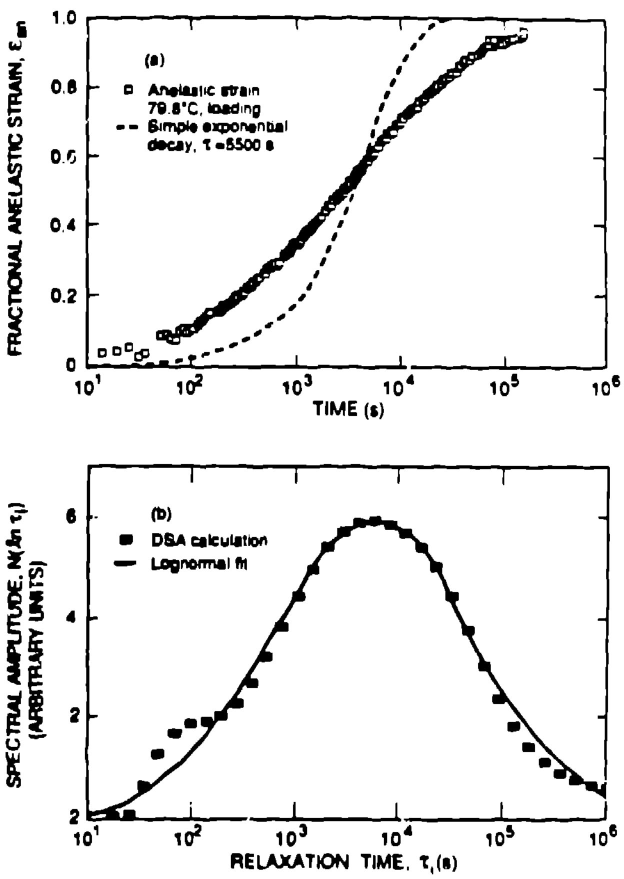

Figure 3. (a) Fractional anelastic strain versus time at 79.8°C. (b) Relaxation time spectrum calculated from the data above.

The value of the distribution parameter obtained from this fit is ß=3.25. This may be compared with the value ß=2.74 which was obtained from our IF study. Nowick and Berry have discussed the predicted temperature dependence of ß for anelastic relaxations [13]. They point out that knowing the temperature dependence of ß, one can distinguish whether a thermally activated relaxation is controlled either by (i) a distribution of activation energies (with a constant pre-exponential frequency factor) or (ii) a distribution of frequency factors (with a constant activation energy). For the latter case the distribution parameter ß is independent of temperature. For the former case if the distribution of relaxation times is lognormal, then there must be a normal distribution of activation energies which broadens with decreasing temperature. For the intermediate case where distributions in both Q and ln(τ_0) occur, the distribution parameter is given by

$$\beta(T) = |\, \beta_0 \pm \beta_Q/kT \,|, \qquad (4)$$

where β_0 and β_Q are the distribution parameters for log(τ_0) and Q, respectively. A fit of our experimental values to Equation 4 yields β_0=0.83 and β_Q=0.077 eV with the second term positive. In the temperature range of this study the values for the second term (which is the one associated with a distribution in Q) ranges from 2.4 to 2.9. Since this is roughly a factor of three greater than $\beta_0=0.83$ for the distribution in $\log(\tau_0)$, this is strong evidence that the distribution in Q dominates this oxygen relaxation in $YBa_2Cu_3O_{7-\delta}$.

B. Temperature dependence of the relaxation time

Values of τ_{infl} for 26 MAE measurements from 50°C to 110°C, both under loading and unloading conditions, are shown in the Arrhenius plot of Figure 4. It may be seen that the relaxation times are the same at a given temperature for both the loading and the unloading experiments. The Arrhenius fit gives $Q=1.09(\pm 0.03)$ eV and $\tau_0=6.5\times10^{-13}$ s. These values are in good agreement with the previously mentioned values of $Q=1.05$ eV and $\tau_0=9.3\times10^{-13}$ s obtained for all prior IF results. The combined MAE and IF results are shown in Figure 5. We note that there is a good fit to the Arrhenius relation over eleven orders of magnitude of relaxation time (a record that approaches the extent of the measurements of the Snoek peak for carbon in iron). Clearly, the same relaxation is being measured by the two different methods. Thus we deduce that the oxygen relaxation has the same rate-limiting step over the entire temperature range from 50°C to 600°C.

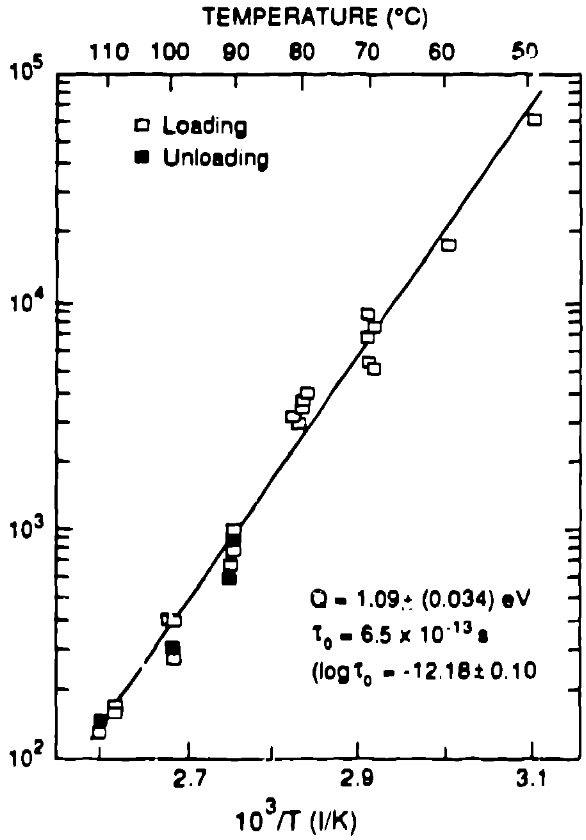

Figure 4. Arrhenius plot of relaxation time of oxygen obtained by mechanical after-effect method.

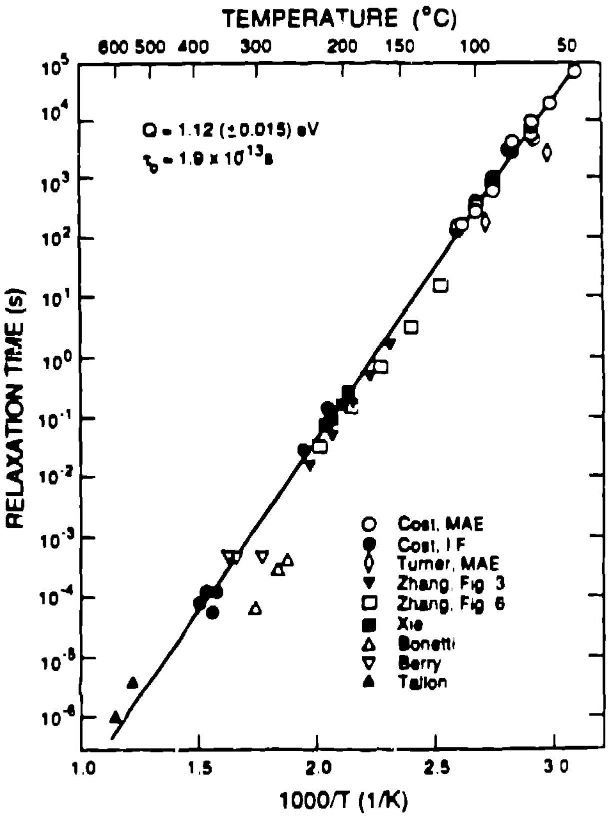

Figure 5. Arrhenius plot of relaxation time of oxygen obtained by anelastic measurements from all investigations on $YBa_2Cu_3O_{7-\delta}$.

C. Comments on the anelastic results

The results of Turner shown in Figure 5 appear to also have been obtained by the MAE method, but this has not yet been confirmed [15].

Rothman and coworkers have studied oxygen diffusion in $YBa_2Cu_3O_{7-\delta}$ using tracer techniques [16]. Their results have been definitive for understanding mass transport of oxygen in bulk $YBa_2Cu_3O_{7-\delta}$. Relationships between oxygen mobility as studied by mass transport methods (e.g., tracer diffusion) as compared to atomic jump methods (e.g., anelastic) has been discussed by Cost and Stanley [8]. An important concept from this discussion is that one need not expect the activation energies as obtained by mass transport and the anelastic techniques to be the same. We now know that for $YBa_2Cu_3O_{7-\delta}$, $Q_{anelastic}=1.12$ eV, while $Q_{diff}=0.97$ eV [16]. This appears to be a true difference, and is understood as follows: Anelastic techniques average single (or only a few) atomic jumps of many atoms. Transport methods, on the other hand, measure a progression of many jumps by the same atom. Atomic jumps occur in a spectrum of local environments and thus have a range of jump rates. The activation energy obtained by anelastic methods depends upon the averaging of the simultaneous jumps, while that obtained by mass transport methods depends upon the average of connected regions of fast jumping, i.e., the faster jump rate portion of the spectrum. Thus, because of this different averaging, we predict $Q_{diff}<Q_{anelastic}$, which is what we now know to be true for the mobility of oxygen in $YBa_2Cu_3O_{7-\delta}$.

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