# Elastic aftereffect study of the ferroelastic tetragonal-orthorhombic phase transition in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub>$ \*

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# **Abstract**

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub> compounds exist in tetragonal and orthorhombic structures. The transition between these structures is a ferroelastic order-disorder phase transformation, caused by a spatial redistribution of the 0 atoms in the  $Cu(1)$  atomic plane. The diffusive jumps of the O, which lead to such a redistribution, induce an anelastic relaxation process. We show that this relaxation process exhibits, in the neighborhood of the tetragonal-orthorhombic phase transformation, a very large increase of both the relaxation strength and the relaxation time (critical slowing down), where the temperature behavior of both quantities is approximately described by a Curie-Weiss law. We discuss finally elastic aftereffect measurements on sintered  $YBa_2Cu_3O_x$  samples which demonstrate the distinct influence of the tetragonai-orthorhombic phase transformation on the relaxation strength and relaxation time.

## **1. Introduction**

Depending on temperature and O concentration  $x$ ,  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>$  compounds exist in tetragonal and orthorhombic phases that reflect different states of order of the O in the Cu(1) atomic plane  $[1-5]$ . Figure 1 presents schematic views of this plane for both the tetragonal and orthorhombic phases. In this plane, the O atoms occupy sites between two Cu atoms where, however, only a fraction  $c = (x - 6)/2$  of all the available sites is actually populated ( $c \le 0.5$  because of  $x \le 7$ ). We can distinguish two types of 0 sites, sites of type 1 where the two nearest neighbor  $Cu$  atoms are in the x-direction, and sites of type 2 where the neighboring Cu atoms



Fig. 1. Schematic view of a Cu(1) atomic plane in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub>$ for the tetragonal and orthorhombic lattice structure [l]. For the orthorhombic structure, the figure shows a preferential occupation of 0 sites with nearest Cu neighbors in the y-direction together with the resulting orthorhombic lattice distortion (the size of the lattice distortion is larger than in reality).

are in the y-direction. In the tetragonal phase, both types of sites are occupied with the same probability c, whereas one of the two types of sites is occupied with higher probability in the orthorhombic structure. The orthorhombic structure in Fig. 1, for instance, shows a preferential occupation of sites of type 2.

The orthorhombic lattice distortion results from the higher population of the 0 sites of one type. The distortion can be described by the strain [6]:

$$
\varepsilon_{ij} = \sum_{\nu=1}^{2} (c_{\nu} - c) \cdot \lambda_{ij}^{(\nu)} = (c_1 - c) \cdot \{\lambda_{ij}^{(1)} - \lambda_{ij}^{(2)}\}
$$

$$
= (c_1 - c_2) \cdot (\lambda_1 - \lambda_2) \cdot (\delta_{\nu} \delta_{\mu} - \delta_{\nu} \delta_{\nu})
$$
(1)

where  $c_v$  is the occupation probability of the sites of type  $v$  or, identically, the number of  $O$  atoms per unit cell, located on sites of type  $v$  (the overall occupation probability  $c = (7-x)/2$  of the sites of both types is  $c = (c_1 + c_2)/2$ . The tensor  $\lambda_i^{(v)}$  characterizes the lattice strain caused by  $O$  atoms on sites of type  $v$ . The nonzero components of  $\lambda_{ij}^{(v)}$  are  $\lambda_{xx}^{(1)} = \lambda_{yy}^{(2)} = \lambda_1$  and  $\lambda_{yy}^{(1)} =$  $\lambda_{xx}^{(2)} = \lambda_2$ , where structural data for the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> system yield  $\lambda_1 - \lambda_2 \approx 0.019$  [2, 7]. This and the relation  $c_1 - c = -(c_2 - c)$  yields the two final terms of eqn. (1) which demonstrate that the only non-zero components of the orthorhombic strain are  $\epsilon_{xx}$  and  $\epsilon_{yy} = -\epsilon_{xx}$ .

The transition between the tetragonal and the orthorhombic structure is a ferroelastic order-disorder phase transformation. The order parameter is proportional either to the orthorhombic strain  $\epsilon_{xx}$  or to the

<sup>\*</sup>Invited paper.

population difference  $c_1 - c$ . The ferroelastic behavior of the transformation follows from the fact that the transition is continuous (or of second order), at least above 440 °C [2]. Deviations from a continuous phase transformation might exist in a limited temperature range around 200 °C, as predicted from theoretical model calculations performed with three parameters for the short-range pair-interaction energy between an O atom and its first, second and third O neighbor, respectively [5]. However, the calculations did not consider the long-range elastic interaction between the O atoms, which contributes  $\sim 10\%$  to the total interaction energy that leads to the phase transformation [8] and may favor a continuous transformation behavior. The low jump rates of the O [9, 10] make it finally difficult to establish true equilibrium conditions in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>4</sub>$ samples so that reliable experimental data on the nature of the phase transformation at and below  $\sim$  200 °C do presently not exist (this holds also for the phase boundary between the various orthorhombic phases with their different O superstructures) [2].

This paper discusses the influence of the ferroelastic tetragonal-orthorhombic phase transformation in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub>$  on anelastic experiments. We shall see that anelastic experiments in the neighborhood of the phase transformation exhibit (i) an extremely large (in fact, diverging) relaxation strength, approximately describable by a Curie-Weiss law, and (ii) a decrease of the relaxation rate, known as critical slowing down [11]. In Section 2, both of these effects will be discussed within a mean-field approximation for the phase transformation. We apply this simple approximation since it demonstrates the basic characteristics of the anelastic relaxation, although it will not yield sophisticated details of the phase transformation itself such as the occurrence of the O superstructures in the various orthorhombic phases. In Section 3, we report experimental results which evidence both the large relaxation strength and the critical slowing down in the neighborhood of the phase transformation.

## **2. Theoretical background**

For the subsequent discussion, we distinguish between O atoms of type 1 or 2, populating sites of type 1 or 2, respectively. This means, for instance, that a diffusive jump of an O atom from a site of type 1 to a site of type 2 corresponds to a chemical reaction that transforms an O atom of type 1 in an O atom of type 2. In this case, thermodynamic equilibrium requires in the absence of external stresses:

$$
\mu_1(c_1, c, T) = \mu_2(c_2, c, T) \tag{2}
$$

where  $\mu_v(c_v, c, T)$  is the chemical potential of O atoms of type  $v$ .

The presence of external stresses  $\sigma_{ik}$  modifies eqn. (2), which now reads (Einstein's summation convention) [61

$$
\mu_1(c',_1, c, T) - v_0 \cdot \lambda_{kl}^{(1)} \sigma_{kl} = \mu_2(c',_2, c, T) - v_0 \cdot \lambda_{kl}^{(2)} \sigma_{kl} \qquad (3)
$$

where  $v_0 \approx 175~\text{\AA}^3$  [1, 2] is the volume of an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> unit cell. The occupation probabilities  $c'_1$  and  $c'_2$  in eqn. (3) differ from the equilibrium values  $c_1$  and  $c_2$ in eqn. (2) because of the stresses  $\sigma_{kl}$ . For small variations  $c'_{1} - c_{1} = -(c'_{2} - c_{2})$ , these variations are obtained from a linear expansion of the chemical potentials in eqn. (3), leading to

$$
c'_{1} - c_{1} = v_{0} \cdot (\lambda_{kl}^{(1)} - \lambda_{kl}^{(2)}) \cdot \sigma_{kl} / \left( \frac{\partial \mu_{1}}{\partial c_{1}} + \frac{\partial \mu_{2}}{\partial c_{2}} \right)
$$
(4)

The stress-induced variation  $c'_{1} - c_{1}$  describes the anelastic strain  $\epsilon_{ij}^{(a)}$  according to eqn. (1). This allows the determination of the relaxations  $\Delta s_{ijkl}$  of the elastic compliance, defined by  $\epsilon_{ij}^{(a)} = \Delta s_{ijkl} \sigma_{kl}$ . The result for the relaxations is

$$
\Delta s_{ijkl} = v_0 \cdot (\lambda_{ij}^{(1)} - \lambda_{ij}^{(2)}) \cdot (\lambda_{kl}^{(1)} - \lambda_{kl}^{(2)}) / \left( \frac{\partial \mu_1}{\partial c_1} + \frac{\partial \mu_2}{\partial c_2} \right)
$$
 (5)

From the fact that the only non-zero components of  $\lambda_{ij}^{(v)}$  are  $\lambda_{xx}^{(1)} = \lambda_{yy}^{(2)} = \lambda_1$  and  $\lambda_{yy}^{(1)} = \lambda_{xx}^{(2)} = \lambda_2$ , the only nonzero relaxations of the elastic compliances are found to be  $\Delta s_{11}$ ,  $\Delta s_{22}$  and  $\Delta s_{12}$  (Voigt's notation [12]). These relaxations can be written as:

$$
\Delta s_{11} = \Delta s_{22} = -\Delta s_{12} = v_0 \cdot (\lambda_1 - \lambda_2)^2 / \left( \frac{\partial \mu_1}{\partial c_1} + \frac{\partial \mu_2}{\partial c_2} \right)
$$
 (6)

Note that there are in total six or nine independent elastic compliances for the tetragonal *(P4/mmm* [1]) and orthorhombic structure, respectively [6, 12].

A quantitative calculation of the relaxation of the elastic compliances according to eqn. (6) requires the knowledge of  $\partial \mu_{v}/\partial c_{v}$  for both types of O atoms. Within a mean-field (or Bragg-Williams) approximation for the tetragonal-orthorhombic phase transformation, the chemical potentials  $\mu$ <sub>v</sub> can be written as [13, 14]

$$
\mu_v = k_{\rm B} T \cdot \ln \frac{c_v}{1 - c_v} - \alpha \cdot (c_v - c) \tag{7}
$$

where  $k_{\text{B}} T$  is the thermal energy. In eqn. (7)  $-k_{\text{B}} \cdot \ln(c_v/$  $(1-c_v)$  is the partial entropy of O atoms of type v occupying their sites without any interaction except for the fact that a given site can be occupied only once. The term with factor  $\alpha$  describes the difference in the (partial) energies of the O atoms of type 1 and type 2, caused by an interaction between O atoms of different type and favoring energetically a preferential occupation of one of the two types of sites (this term is responsible for the phase transformation). The condition  $\mu_1 = \mu_2$ leads to the equation

$$
\frac{c_1 \cdot (1 - c_2)}{c_2 \cdot (1 - c_1)} = \exp\left\{\frac{2\alpha \cdot (c_1 - c)}{k_B T}\right\} \tag{8}
$$

from which the equilibrium occupation probabilities  $c_1$ and  $c_2 = 2c-c_1$  can be calculated according to standard procedures [13, 14]. The calculation yields  $c_1 = c_2 = c$ for temperatures above a critical temperature

$$
T_c = \alpha c \cdot (1 - c) / k_B \tag{9}
$$

so that the system is tetragonal above  $T_c$ . Below  $T_c$ , on the other hand, the occupation probabilities  $c_1$  and  $c_2$  differ from c, so that the system is in its orthorhombic phase. Figure 2 presents, for the example  $c = 0.25$  (which corresponds to  $x=6.5$ ), the difference  $c_1 - c$  in a plot  $vs. T/T_c$ , as calculated according to eqn. (8) (it was already mentioned that  $c_1-c$  is proportional to the order parameter).

The critical temperature  $T_c$  depends on c and, therefore, on the  $O$  concentration  $x$ . The concentration dependence, as expressed by eqn. (9), describes essentially correctly the experimentally determined phase boundary between the tetragonal and the orthorhombic structure (the maximum  $T_c$  exists for  $c=0.5$ , or for  $x=7$ ) [15-17]. From  $T_c \approx 400$  °C for  $x=6.5$  [15-17], the parameter  $\alpha$  can be estimated to be  $\alpha \approx 0.18$  eV.

From the above expression for  $\mu_v$  and with eqn. (9) for  $T_c$ , the relaxations of the elastic compliances in eqn. (6) can be written in the general form

$$
\Delta s_{11} = \Delta s_{22} = -\Delta s_{12} = F_1 \cdot \frac{c \cdot (1 - c) \cdot v_0 \cdot (\lambda_1 - \lambda_2)^2}{2k_B T}
$$
 (10)

where factor  $F_1$  is given by

$$
F_1 = T / \left[ \frac{T}{2} \cdot \left( \frac{c(1-c)}{c_1(1-c_1)} + \frac{c(1-c)}{c_2(1-c_2)} \right) - T_c \right]
$$
 (11)



Fig. 2. The magnitude of the difference  $c_1-c$  (left-hand scale) and the factors  $F_1$  and  $F_2$  (right-hand scale) in a plot *vs.*  $T/T_c$ . The broken line shows the value  $F_1 = F_2 = 1$  found for  $\alpha = 0$  or  $c \rightarrow 0$  (i.e. in the absence of the phase transformation). The data are valid for  $c = 0.25$ , which corresponds to an O concentration  $x=6.5$ . For more details, see the text.

For a discussion of the results in eqns. (10) and (11), we consider first temperatures above  $T_c$ . This case implies  $c_1 = c_2 = c$ , so that  $F_1$  can be written as  $F_1 = T/$  $(T-T_c)$ . We find, accordingly, a Curie-Weiss law for the relaxations of the elastic compliances, demonstrating a ferroelastic behavior of the phase transition which causes extremely large relaxations closely above  $T_c$ . We find further  $F_1 = 1$  in the absence of the phase transformation *(i.e.* for  $\alpha = 0$  or for  $c \ll 1$ , since both cases lead to  $T_c \rightarrow 0$ ). In this case, the relaxations of the elastic compliances in eqn. (10) become identical to standard literature results [6].

For temperatures below  $T_c$ , a calculation of the relaxations of the elastic compliances according to eqns. (10) and (11) requires first a determination of the equilibrium values of the occupation probabilities  $c_1$ and  $c_2$  with the help of eqn. (8). The analysis also shows that in this case the relaxations become extremely large in the neighborhood of the phase transformation. To demonstrate this effect in more detail, we present in Fig. 2 factor  $F_1$  in a plot *vs. T*/T<sub>c</sub>, again calculated for the concentration  $c = 0.25$ . The figure shows clearly the large increase of this factor, which determines the size of the relaxation, in the neighborhood of the critical temperature  $T_c$ .

The above considerations are valid for small stressinduced variations of the occupation probabilities  $c_1$ and  $c_2$ . This restriction is of importance for temperatures below  $T<sub>e</sub>$  since, in this case, sufficiently large stresses can induce variations of the occupation probabilities which change the sign of  $c_1-c$  and, consequently, the sign of the orthorhombic lattice distortion (or of the order parameter). In fact, the application of stresses turned out to be a successful technique in order to suppress twinning in  $YBa_2Cu_3O_x$  single crystals [18]. It is obvious that the present results cannot describe such a situation. We mention finally, previous theoretical work on the anelastic relaxation in the temperature range below  $T_c$  [19]. This work used a low-concentration approximation in calculating the O distribution between the two types of sites, which is certainly not justified in the present case, and it did not account for the fact that the energy difference between the O atoms on sites of types 1 and 2 is a function of the occupation probabilities  $c_1$  and  $c_2$  (this functional dependence is actually the reason for the phase transformation). It is, accordingly, doubtful whether the results are really applicable to the  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>$  system.

The influence of the phase transformation on the relaxation time  $\tau$  will be described by the equation

$$
\frac{dc''_1}{dt} = \frac{1}{2\tau^{(\alpha=0)}} \cdot \left\{ c''_2(1-c'') \cdot \exp\left(\frac{\alpha(c''_1 - c)}{k_B T}\right) - c''_1(1-c''_2) \cdot \exp\left(-\frac{\alpha(c''_1 - c)}{k_B T}\right) \right\}
$$
(12)

for the changes of the occupation probabilities  $c_{1}^{n}$  and  $c''_2$  with time t, caused by diffusive jumps of the O atoms in the Cu(1) plane (note that  $dc''_1/dt = -dc''_2/$ dt). The equation states that  $dc''_1/dt$  is proportional to the expression in the braces, with  $\tau^{(\alpha=0)}$  as a proportionality constant that later will turn out to be the relaxation time for  $\alpha = 0$  or  $c \rightarrow 0$  *(i.e.* in the absence of a phase transformation). The first term of the expression in the braces describes the rate of O atoms jumping from sites of type 2 to sites of type 1, whereas the reverse rate is given by the second term. The first term is proportional to the number of O atoms on sites of type 2, *i.e.* to  $c''_2$ , and to  $1-c''_1$  since an O atom can only jump to a vacant site. The factor  $c''_1(1-c''_2)$  of the second term stands for the analogous relationship there. The exponential functions account for the fact that the difference in the (partial) energies of the O atoms on sites of type 2 and sites of type 1 is  $2\alpha(c''_1 - c)$ , as given by the chemical potential in eqn. (7). This implies, for reasons of detailed balance, the presence of the two exponential functions in eqn. (12).

For  $dc''_1/dt=0$ , eqn. (12) describes an equilibrium situation. It is readily seen that, in this situation, the occupation probabilities  $c_{1}$  and  $c_{2}$  in eqn. (12) exhibit the same relationship as  $c_1$  and  $c_2$  in eqn. (8). This fact shows the internal consistency of the present model calculations for relaxation strength and relaxation time.

For small deviations of  $c''_1$  from the equilibrium value  $c_1$  (according to eqn. (8)), the relaxation process in eqn. (12) can be described by a linear expansion with respect to  $\Delta c_1 = c''_1 - c_1$ . The expansion yields the result

$$
\frac{\mathrm{d}c''_1}{\mathrm{d}t} = \frac{\mathrm{d}\Delta c_1}{\mathrm{d}t} = -\frac{\Delta c_1}{\tau} \tag{13}
$$

where the relaxation time  $\tau$  is given by

$$
\tau = F_1 \cdot \frac{c(1-c)}{\sqrt{c_1 c_2 (1-c_1)(1-c_2)}} \cdot \tau^{(\alpha=0)} = F_2 \cdot \tau^{(\alpha=0)} \tag{14}
$$

Equation 14 shows that the relaxation time  $\tau$  becomes identical to  $\tau^{(\alpha=0)}$  for  $\alpha=0$  or  $c\rightarrow 0$  *(i.e.* in the absence of the phase transformation). In the general case, however,  $\tau$  differs from  $\tau^{(\alpha=0)}$  by the factor  $F_2 \neq 1$ . Considering first the temperature range above  $T_c$ , where  $c_1 = c_2 = c$ , we find that  $F_2$  is identical to  $F_1$ . This yields, similarly as for the relaxation of the elastic compliances, a Curie-Weiss law  $\tau = \tau^{(\alpha=0)}$ . *T/(T-T<sub>c</sub>)* for the relaxation time, demonstrating the critical slowing down of the dynamics of the relaxation process. An analysis for temperatures below  $T_c$  shows that, in this case, the relaxation time  $\tau$  is larger than  $\tau^{(\alpha=0)}$  in the neighborhood of  $T_c$ , whereas it becomes smaller than  $\tau^{(\alpha=0)}$ at lower temperatures. As an example for the temperature behavior of the relaxation time, we present in Fig. 2 the factor  $F_2$  in a plot *vs. T*/T<sub>c</sub>, again calculated for  $c=0.25$ . The figure shows drastically the increase of the relaxation time in the neighborhood of the phase transformation, and it demonstrates in particular that, in this neighborhood, a large relaxation of the elastic compliances is correlated with a large increase of the relaxation time. We shall see later that this correlation is substantiated in our experimental data.

### **3. Experimental results**

Results of previous anelastic studies on  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>$ samples can be found in recent papers [9, 10, 20–23], and in references therein. The studies that were carried out in the neighborhood of the tetragonal-orthorhombic phase transformation indicate in fact large relaxation strengths  $\Delta$ , in one particular example as large as  $\Delta \approx 0.75$ [9]. A critical slowing down of the relaxation dynamics, on the contrary, has not been discussed in literature so far.

In the following, we present results of (quasistatic) elastic aftereffect experiments on two sintered (polycrystalline) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> samples with  $x \approx 6.29$  and 6.41, carried out in the temperature range between 100 and 150 °C. In this temperature range, both samples were close to the tetragonal-orthorhombic phase transformation. Literature data for the phase boundary [15, 16] seem to indicate that the sample with the lower or higher x were likely to be in the tetragonal or orthorhombic phase, respectively. However, we have mentioned already that the nature of the phase transformation is, in the present temperature range, experimentally not really established, a fact which also leaves uncertainties with respect to the actual behavior of the phase boundaries.

In our experiments, we determined time-dependent deflections of our  $\sim 0.7$  mm thick,  $\sim 5$  mm wide and  $\sim$  45 mm long YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> samples. The investigated sample was fixed at one end in a clamp, and the movement of the other sample end against a counterelectrode was monitored with the help of a capacitance bridge. We probed, accordingly, the relaxation of Young's modulus. The sample preparation, the apparatus, the experimental technique and the data evaluation were similar to a previous study [9]. An improvement in comparison to this study was that the sample was deflected under constant stress conditions which simplified the quantitative data analysis. We mention finally that O losses of our samples, which were in vacuum in the course of the measurements, did not occur because of the low O diffusivity at and below 150 °C [9, 10], and that all our measurements demonstrated a completely reversible relaxation behavior.

Figure 3 shows the deflection and, therefore, the strain of the sample with  $x \approx 6.41$  *vs.* time during measurement at 120 °C. Between times  $t_1$  and  $t_2$  (upper abscissa), the sample was deflected by a constant force, yielding the strain  $\epsilon = \epsilon^{(e)} + \epsilon^{(a)}$  where  $\epsilon^{(e)}$  and  $\epsilon^{(a)}$  are the elastic and the anelastic strain, respectively. After the force was removed at  $t_2$ , the remaining  $\epsilon^{(a)}$  relaxed slowly towards zero.



Fig. 3. The strain  $\epsilon = \epsilon^{(c)} + \epsilon^{(a)}$  of the sample with  $x = 6.41$  during measurement at 120 °C in a plot *vs.* time *t*. The deflecting force was applied between  $t_1$  and  $t_2$ . The insert shows  $\epsilon$  during the first five seconds after  $t_2$ . For more details, see text.



Fig. 4. The ratio  $\epsilon/\epsilon^{(e)}$  after time  $t_2$  in a plot *vs*. the logarithm of time t, measured at 120 °C on the sample with  $x=6.41$  after the deflecting force was applied for four different time periods  $t_2-t_1$ . The figure shows also the values of  $t_2-t_1$ .

Figure 4 presents the results of four measurements, performed at 120 °C on the sample with  $x \approx 6.41$ . The figure shows the anelastic strain  $\epsilon = \epsilon^{(a)}$  after  $t_2$  in a plot *vs.* the logarithm of time, as determined after four different time periods  $t_2-t_1$  for the application of the deflecting force. It can be seen that the values of  $\epsilon^{(a)}$ increase with increasing  $t_2 - t_1$ , thus demonstrating that the time periods  $t_2 - t_1$  do not greatly exceed the involved relaxation times.

It is readily found from Fig. 4 that the time dependence of the anelastic relaxation  $\epsilon^{(a)}$  cannot be described by a single relaxation time. For that reason, we considered for our data a large number of relaxation modes i, characterized by relaxation times  $\tau_i$ , partial relaxation strengths  $\delta_i$  and a total relaxation strength  $\Delta = \sum_i \delta_i$ . We assumed (i) a common pre-exponential factor  $\tau_0$ for the relaxation times  $\tau_i = \tau_0 \exp(H_i/k_B T)$  and (ii) partial relaxation strengths  $\delta_i$  varying with  $H_i$  according to a gaussian distribution centered at  $H_0$  and exhibiting a standard deviation  $\sigma_H$ . We made fits to our data under these assumptions, accounting explicitly for the strain relaxation between  $t_1$  and  $t_2$ . For a given sample and temperature, all the measurements were simultaneously analyzed in a single-fit procedure, where the relevant fit parameters were the total relaxation strength  $\Delta$ , the central relaxation time  $\tau = \tau_0 \exp(H_0/k_B T)$  and the standard deviation  $\sigma_H$ . The solid lines in Fig. 4 represent the fit curves to the data there, and it can be seen that these curves provide a fair description of the data.

Our fits to the 120 °C data yielded central relaxation times  $\tau$ , relaxation strengths  $\Delta$  and standard deviations  $\sigma_H$  as indicated in Table 1. The table shows also the activation enthalpies  $H_0$  resulting from our measurements at 100 and 150 °C, together with the corresponding results for a previously investigated sample  $(x \approx 6.45)$ [9].

The results in Table 1 agree with literature values [9, 10, 20-23] if we account for the considerable scatter of the data. The large relaxation strengths of the samples with  $x \approx 6.41$  and 6.45 are, in fact, expected in the neighborhood of the phase transformation. However, probably the most important result of the present study is the correlation between the central relaxation time  $\tau$  and the relaxation strength  $\Delta$  of the samples in Table

TABLE 1. Results for  $\Delta$ ,  $\tau$ ,  $\sigma_H$  and  $H_0$  obtained from the two samples of this study and from the sample of a previous investigation [9]

O concentration $x$ and experiment	at 120 $^{\circ}$ C	$\tau(s)$ at 120 $^{\circ}$ C	$\sigma_H$ (eV) at 120 $^{\circ}$ C	$H_0$ (eV)
$6.29$ (this study)	$0.06 + 0.01$	$3 + 0.5$	$0.06 + 0.01$	$1.1 \pm 0.3$
$6.41$ (this study)	$0.49 + 0.07$	$98 + 15$	$0.10 + 0.01$	$1.25 + 0.3$
$6.45$ [9]	$0.75 + 0.15$	$700 + 70$	$0.07 + 0.01$	~1.0

1, evidenced by the fact that a larger  $\Delta$  also implies a larger  $\tau$ . According to our discussion in Section 2 (and to Fig. 2), such a correlation is precisely what is predicted in the neighborhood of the tetragonal-orthorhombic phase transformation. The present results for  $\Delta$  and  $\tau$ , and the correlation between these quantities, demonstrates, therefore, convincingly the influence of the ferroelastic phase transformation in  $YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub>$  on the anelastic relaxation behavior.

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