PHYSICAL REVIEW B VOLUME 56, NUMBER 21 1 DECEMBER 1997-I

Pressure-dependent oxygen ordering in strongly underdoped $YBa_2Cu_3O_{7-y}$

Sascha Sadewasser, Yong Wang, and James S. Schilling
Department of Physics, Washington University, C. B. 1105, One Brookings Drive, St. Louis, Missouri 63130

Hong Zheng, Arvydas P. Paulikas, and Boyd W. Veal
Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

(Received 24 July 1997)

Previous studies on the high-T_c superconductor $Tl_2Ba_2CuO_{6+\delta}$ have given evidence for distinct low- and high-temperature oxygen ordering processes activated for temperatures above 13 and 200 K, respectively. In contrast, the present experiments on strongly underdoped $YBa_2Cu_3O_{6.41}$ with $T_c(0) \simeq 13$ K reveal only high-temperature relaxation processes with a relaxation time τ at 298 K which increases under pressure from approximately 10 h at 1 bar to 50 h at 0.79 GPa to 550 h at 2.3 GPa. From these results the activation volume is estimated to be 4.2 cm^3/mol, a value equal to three-quarters of the molar volume of the O^{2-} ion. [S0163-1829(97)06345-5]

I. INTRODUCTION

It is well established that the transition temperature T_c in high-temperature superconductors may depend strongly on both the *content* and the *arrangement* of oxygen defects in the lattice.[1,2] The latter effect was observed by Veal *et al.*[2] in $YBa_2Cu_3O_{7-y}$ (YBCO) who varied the degree of order in the oxygen sublattice through suitable heat treatment, changing T_c by more than 20 K. These results were analyzed in terms of a simple model[3] in which the valence of the Cu(1) ions in the chains, and thus the concentration of charge carriers in the CuO_2 planes, depends on the local coordination of Cu(1) to surrounding oxygen defects. Soon thereafter it was shown by Sieburger and Schilling[4] for $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) that the degree of oxygen order is also a sensitive function of hydrostatic pressure, if the pressure is applied at room temperature (RT). Subsequent studies by Fietz *et al.*[5] confirmed the existence of analogous pressure effects in YBCO; the relaxation time for both thermal-[2] and pressure-induced[6] relaxation effects in YBCO was found to lie in the range 1–10 h (activation energy $E_A \simeq 0.91$ to 0.97 eV) for oxygen deficiencies $y = 0.3$ to 0.6, respectively. Tracer diffusion experiments[7] at RT on YBCO yield $E_A \simeq 0.97$ eV when determined over a range of oxygen stoichiometries.

In view of the high sensitivity of the value of T_c to the degree of local oxygen order in both YBCO and Tl-2201, it is important both from practical and fundamental standpoints to clearly establish in which high-T_c systems, and under what circumstances, oxygen ordering effects play a significant role. It is not widely appreciated that these relaxation effects can be easily overlooked since the temperature must be carefully chosen so as to match the relaxation time τ to the time scale of the experiment. Changing the degree of oxygen ordering through heat treatment or application of pressure represent mutually complimentary techniques.

In addition to pressure-induced oxygen relaxation at RT, Klehe *et al.*[8] found evidence in Tl-2201 for significant relaxation effects at low temperatures (50–100 K). Subsequent studies to higher pressure in a diamond-anvil cell by Looney *et al.*[9] revealed, in fact, that this low-temperature relaxation persists down to temperatures as low as 13 K, and perhaps lower. The data show clearly that there are two distinct relaxation mechanisms: a ‘‘fast’’ process with relatively low activation energy ($E_A \leqslant 0.25$ eV) responsible for the low-temperature relaxation, and a second ‘‘slow’’ process ($E_A \approx 1$ eV) which becomes important near RT. Since the magnitude of either relaxation process is a sensitive function of the content of interstitial oxygen, it is highly likely that both have their origin in rearrangements within the interstitial oxygen sublattice. We have suggested that the low-temperature relaxation may originate from the oscillation of a given interstitial oxygen defect between two equivalent sites within the Tl_2O_2 double-layer in a single unit cell,[8,9] whereas the high-temperature relaxation arises from long-range diffusive motion of the interstitial oxygen.[4]

It is clearly of interest to determine whether or not YBCO also exhibits oxygen relaxation effects at low temperatures. Internal friction studies[10] on YBCO have revealed relaxation peaks in the range 0.08–0.2 eV which would yield very short relaxation times, even at low temperatures ($\sim 10^{-6}$ s at 60 K); this has prompted us to suggest[8] that transient photoinduced superconductivity in this compound may originate from oxygen relaxation processes. Recent studies by Guimpel *et al.*[11] show that thermally induced oxygen ordering and persistent photoconductivity have a common physical origin in the rearrangement of oxygen anions. In the previous high-pressure studies by Fietz *et al.*[5,6] on YBCO the pressure was changed at temperatures near 90 K which precludes the identification of possible relaxation processes at temperatures lower than 90 K. In addition, since the measurement of T_c itself involves a slow temperature sweep (30 min) through the temperature range within ± 5 K of T_c, the sample is effectively annealed at this temperature, precluding the study of relaxation effects at temperatures lower than T_c. If the value of T_c is used to study relaxation effects at low temperature, therefore, a sample with as low a T_c value as possible should be chosen.

In this paper we report the results of a search for low-temperature relaxation phenomena in YBCO to temperatures as low as 14 K. To this end we have selected a homogeneous single crystal of $YBa_2Cu_3O_{6.41}$ with $T_c \simeq 13$ K at ambient pressure. In contrast to the results for Tl-2201, we find no evidence whatsoever for relaxation effects in YBCO for temperatures between 14 and 250 K; relaxation sets in rapidly for temperatures above 250 K. In addition, we find the relaxation time to increase significantly with pressure.

II. EXPERIMENTAL

The sample studied in the present experiments is a single crystal of $YBa_2Cu_3O_{7-y}$ (right-angle parallelopiped with dimensions $1 \times 1 \times 0.26$ mm^3 and mass 1.65 mg). The crystal was grown in air in a gold crucible using the conventional ''self-flux'' procedure from a mixture containing Y:Ba:Cu in the ratios 5:27:68. The sample was cooled from 980 to 930 °C at 0.2 and at 0.4 °C/h from 930 to 880 °C. The oxygen content was subsequently adjusted by heat treating the crystal for 309 h at 520 °C in a flowing gas mixture of 0.113% O_2 in N_2. The oxygen pressure was continuously monitored using a zirconia-cell oxygen pressure monitor manufactured by Ametek, Inc. After the equilibration in O_2/N_2, the sample was quenched into liquid nitrogen. This procedure produces a sample with $T_c \simeq 13$ K and with oxygen stoichiometry $7\text{-}y = 6.41$, as established with prior calibration studies.[12] To obtain a room-temperature equilibrium oxygen vacancy ordered condition, the sample was aged at room temperature $(295 \pm 1$ K) for over two months before measurements were performed.

The He-gas pressure system (Harwood) used in this study is capable of reaching hydrostatic pressures to 1.4 GPa. The CuBe pressure cell (Unipress) is inserted into a two-stage closed-cycle refrigerator (Leybold) which operates in the temperature range 2–320 K. The pressure in the pressure cell can be changed at any temperature above the melting curve T_m (Ref. 13) of the pressure medium He (for example, $T_m = 13.8$ K at 0.1 GPa and $T_m = 52.4$ K at 0.8 GPa). The pressure decrease upon cooling is kept to below 20% by the introduction of an appreciable ''dead volume'' at RT.

The superconducting transition is measured by the ac susceptibility technique using a miniature primary/secondary coil system located inside the 7 mm I.D. bore of the He-gas pressure cell. In the present studies a magnetic field of 1.1 Oe (rms) at 507 Hz is applied along the c axis (short dimension) of the crystal perpendicular to the CuO_2 planes. From the sample dimensions given above, the demagnetization factor is calculated to be $\mathcal{D} = 0.64$.[14] Details of the experimental setup are given elsewhere.[15]

III. RESULTS OF EXPERIMENT

A. First measurement series

Three consecutive series of high-pressure measurements (labeled A, B, and C) were carried out on the $YBa_2Cu_3O_{6.41}$ single crystal to hydrostatic pressures at RT of 0.10, 0.79, and 0.57 GPa, respectively. At temperatures near T_c these pressures decrease to 0.09, 0.65, and 0.46 GPa, respectively, due to the contraction of He upon cooling. Results of the first (A) series of experiments are shown in Fig. 1 where the real χ' and imaginary χ'' parts of the ac susceptibility are plotted versus temperature. The transition widths are seen to be quite narrow for such a strongly underdoped sample, underscoring the good sample homogeneity. The size of the superconducting transition is large and would be consistent with full shielding $(\Delta\chi' = -1/4\pi)$ for a demagnetization factor of $\mathcal{D} = 0.66$,[16] in excellent agreement with the value $\mathcal{D} = 0.64$ derived from the sample geometry.[14] We arbitrarily take the midpoint of the superconducting transition in χ' to define the value of T_c. The superconducting onset was also monitored and found to shift by the same amount as the midpoint following changes in pressure, annealing time or annealing temperature. The changes in T_c could be determined to the highest accuracy (better than ± 30 mK) by shifting the transition curves along the temperature axis until overlap occurs.

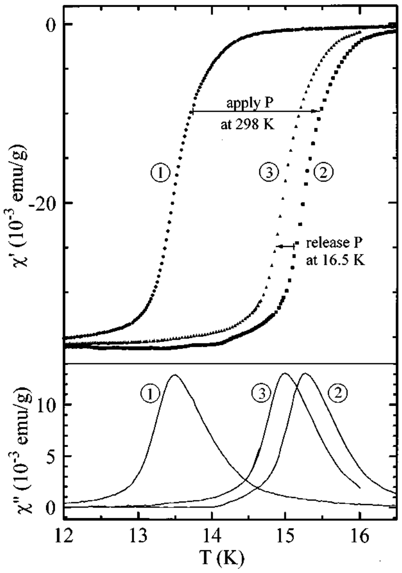

FIG. 1. Real χ' and imaginary parts χ'' of the ac susceptibility of $YBa_2Cu_3O_{6.41}$ at 1.1 Oe (rms). Encircled numbers give order of measurement. Applying 0.10 GPa pressure at 298 K shifts T_c from 13.5 K (●) to 15.3 K (■) after 17 h annealing. T_c decreases to 15.0 K (▲) after fully releasing the pressure at 16.5 K.

As seen in Fig. 1, the transition temperature of the crystal at ambient pressure is equal to $T_c(0) = 13.5$ K (curve 1) following a two month storage at the temperature 295 ± 1 K. A pressure of 0.10 GPa was then applied at 298 K (0.09 GPa at low temperature) and the sample was retained at this temperature for 17 h to allow the oxygen ordering to reach equilibrium[17] before cooling down at the highest possible rate (3–5 K/min) to measure $T_c = 15.3$ K (curve 2). The very large value of the pressure derivative obtained, $dT_c/dP \approx +20$ K/GPa, is in reasonable agreement with earlier studies by Fietz *et al.*[6] After releasing the pressure fully at 16.5 K, 4 K above the melting temperature of He at 0.09 GPa,[13] T_c was immediately remeasured and found to have decreased to $T_c = 15.0$ K (curve 3 in Fig. 1). The sample was then warmed up rapidly to consecutively higher annealing temperatures $T_{\rm anneal}$, annealed there for 1 h, and then cooled down to remeasure T_c. Within experimental error, no further change in T_c is observed for annealing temperatures as high as 264 K, as seen in Fig. 2. In this experiment, therefore, we find no evidence for relaxation phenomena at low temperatures; this is one of the main results of the present paper.

Following the 1 h anneal at 280 K (pt 18), the relaxation in T_c is determined for various cumulative annealing times

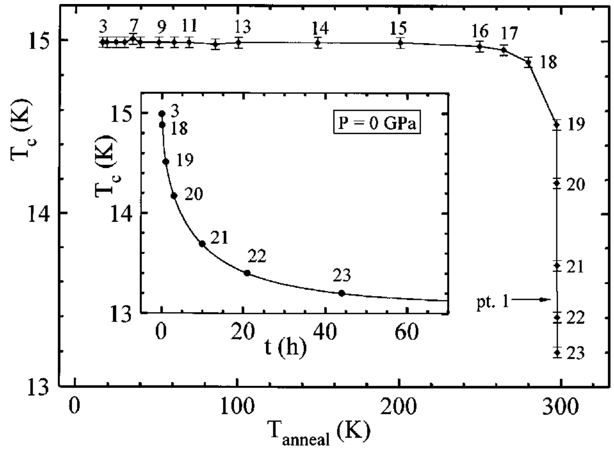

FIG. 2. Dependence of T_c for $YBa_2Cu_3O_{6.41}$ on the annealing temperature (series *A*) following the application of 0.10 GPa pressure at 298 K and its full release at 16.5 K. Numbers give order of measurement. The solid line is a guide to the eye. Inset shows the time dependence of T_c after fully releasing the pressure at 16.5 K.

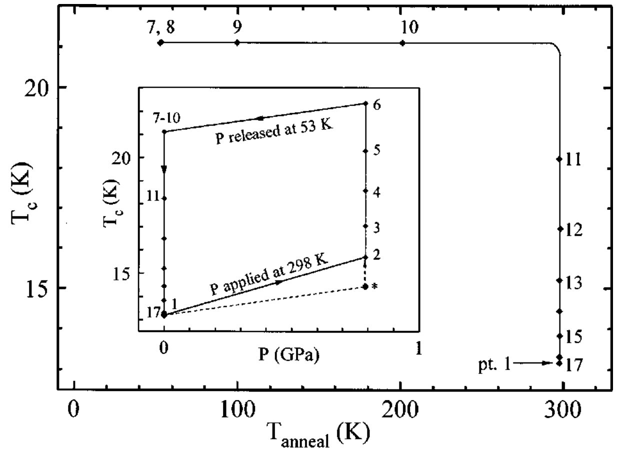

FIG. 3. Dependence of T_c for $YBa_2Cu_3O_{6.41}$ on the annealing temperature (series *B*) following (inset) the application of 0.79 GPa pressure at 298 K and its release at 53 K. Numbers give order of measurement. Solid lines are guides to the eye. See text for meaning of the asterisk (*) point.

(1, 3, 10, 21, 44 h) at the fixed temperature 298 K (pts 19 to 23) (see inset to Fig. 2). The fit to these data given by the solid line will be discussed below in the ''analysis'' section. An estimate of the relaxation taking place while the sample is warmed up to 298 K and cooled down again gives a change in T_c of less than 15 mK. This effect is smaller than the experimental uncertainty and will thus be neglected.

For pts 22 and 23 in Fig. 2, T_c is seen to relax back *past* its initial value for pt 1 [$T_c(0) = 13.5$ K]. The reason for this behavior is the fact that, prior to measuring pt 1, the sample had been stored for two months at 295 ± 1 K. Prior to measuring pt 23, however, the sample had been annealed at the higher temperature of 298 K for 44 h. The equilibrium state in the oxygen sublattice at 298 K contains a higher degree of disorder than at 295 K, leading to the lower value of T_c. To check this explanation, after pt 23 we annealed the sample for 19 h at 293 K; T_c was observed to shift back up in temperature by 0.3 K from 13.2 to 13.5 K. According to Veal *et al.*,[2] if the storage temperature of an underdoped YBCO sample with $T_c \approx 13$ K is decreased by 5 K, the enhanced order in the oxygen sublattice would result in an increase in T_c by approximately 0.4 K, in excellent agreement with our present findings. Following measurement series *A*, the sample was annealed at ambient pressure at 298 K for two days to bring the sample back into its equilibrium state.

B. Second measurement series

To explore the possibility that pressures higher than 0.10 GPa might be required to excite low-temperature relaxation processes, a pressure of 0.79 GPa was then applied at 298 K (measurement series *B*) and held at that temperature for consecutive time intervals up to 34 h total, raising T_c from 13.2 to 22.4 K, as seen in the inset to Fig. 3 (pts 1–6). The dependence of T_c on annealing time after the application of 0.79 GPa pressure is shown in Fig. 4(a).

The pressure was then fully released at 53 K, a temperature 5 K above the melting curve of He;[13] T_c was then immediately remeasured and found to have decreased from 22.4 to 21.1 K. Annealing the sample at 53 K for 3 h resulted in no further change in T_c (pt 8). Also subsequent annealing at 100 and 200 K for 1 h resulted in no measurable change in T_c, as seen in Fig. 3. As for the previous measurement to 0.10 GPa, no low-temperature relaxation phenomena were observed to 0.79 GPa pressure for the present YBCO sample. High-temperature relaxation was observed by annealing the sample at 298 K for consecutively longer time periods to 87 h total, as seen in Figs. 3 and 4(b) (pts 11–17). Following this 87 h anneal at 298 K, the T_c value is seen to revert back to within 40 mK of the initial value (13.2 K) for pt 1.

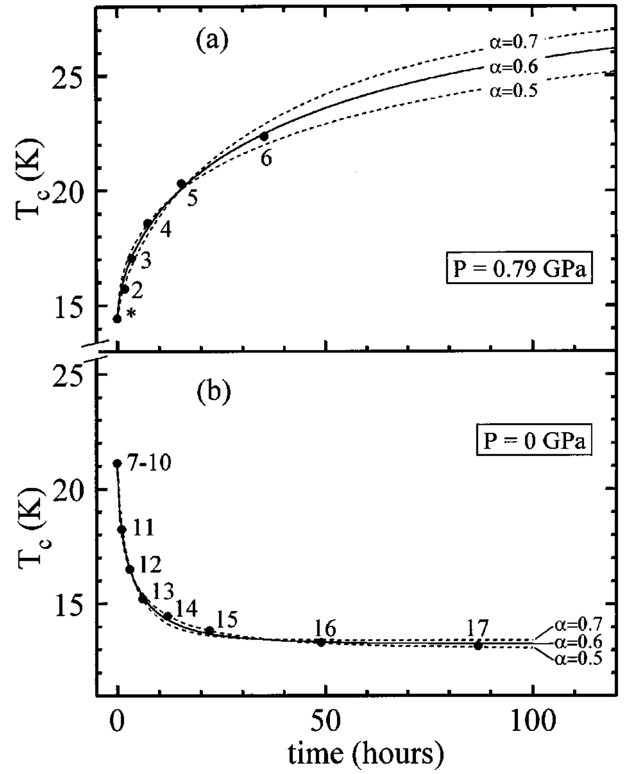

FIG. 4. Relaxation data at 298 K in series *B* at (a) 0.79 GPa and at (b) ambient pressure. Lines are best fits to data using Eq. (2) for different values of α. See text for meaning of the asterisk (*) point.

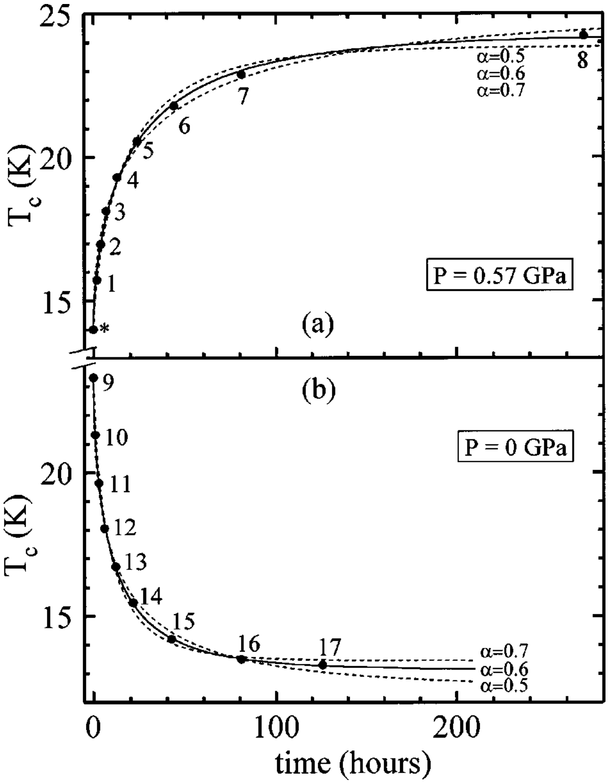

FIG. 5. Relaxation data at 298 K in series C at (a) 0.57 GPa and at (b) ambient pressure. Lines are best fits to data using Eq. (2) for different values of α. See text for meaning of the asterisk (*) point.

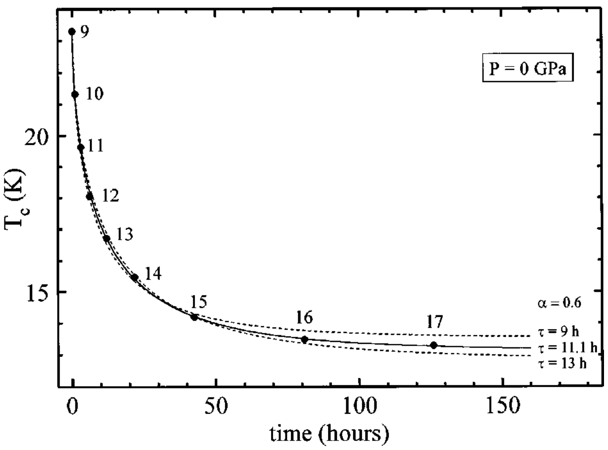

FIG. 6. Relaxation data at 298 K in series C at ambient pressure fitted to Eq. (2) for $\alpha=0.6$ using different relaxation times τ.

From a visual inspection of the data in Figs. 4(a) and 4(b) it is immediately evident that the relaxation of T_c proceeds more slowly following the *application* of pressure than the *release* of pressure, i.e., the relaxation time τ increases if the lattice is compressed. The more detailed analysis in the following section ''analysis of relaxation data'' confirms this assertion. The measurement series A and B (Figs. 2 and 4) reveal that the relaxation data, particularly those under pressure, must be carried out for very long periods of time (many days) to allow T_c to reach its true equilibrium value. Pt 6 in Fig. 4(a), which was taken after a 34 h annealing time, is evidently quite far from its equilibrium value.

Following this measurement series (B), the results of measurement series A were checked by applying 0.10 GPa pressure at 298 K and releasing it fully at 14 K. No low-temperature relaxation in T_c was observed for temperatures above 14 K.

C. Third measurement series

In the third experiment (measurement series C) the goal was to allow sufficient time following pressure changes for the sample to reach full thermal equilibrium. The sample was first annealed at 298 K at ambient pressure for 38 h before 0.57 GPa pressure was applied over a 35 min period. The sample was then annealed at 298 K under this pressure for 45 min before being cooled down at the maximum rate to measure T_c [pt 1 in Fig. 5(a)]. The relaxation in T_c at the 0.57 GPa pressure was then measured as a function of the annealing time at 298 K up to a maximum time of 269 h (more than 11 days). The pressure was then fully released at 45 K and the sample immediately cooled down to determine T_c (pt 9). The relaxation of T_c at ambient pressure was then measured for consecutively longer annealing times at 298 K to a maximum time of 126 h [pts 10–17 in Fig. 5(b)]. The analysis of the relaxation data is presented in the following section.

IV. ANALYSIS OF RELAXATION DATA

We now proceed with an analysis of the time-dependent relaxation data in Figs. 2, 4, 5, and 6. In conventional superconductors the transition temperature is a single-valued function of pressure, $T_c=T_c(P)$, which does not, unless phase changes occur, depend on the temperature at which the pressure is changed or the detailed thermal history of the sample; as the pressure changes, T_c varies instantaneously. As we have seen, this is not true for selected oxide superconductors such as Tl-2201 and YBCO. In these systems the total pressure dependence of T_c can be separated into two components

$$\frac{dT_c}{dP}=\left(\frac{dT_c}{dP}\right)_{\text{intrinsic}}+\left(\frac{dT_c}{dP}\right)_{\text{OO}}, \qquad (1)$$

the first giving the ''intrinsic'' change in T_c which occurs instantaneously following changes in pressure, and the second ''oxygen ordering'' (OO) pressure derivative which

TABLE I. Fit parameters for measurement series A used in Fig. 2. The optimal values are given in boldface type.

P (GPa)	$T_c(\infty)$ (K)	$T_c(0)$ (K)	τ (h)	α	Error χ^2
0	12.82	14.99	13.11	0.5	0.0019
0	**13.08**	**14.99**	**7.92**	**0.6**	**0.0001**
0	13.20	14.99	6.34	0.7	0.0013

TABLE II. Fit parameters for measurement series B used in Figs. 3 and 4. The optimal values are given in boldface type.

P (GPa)	$T_c(\infty)$ (K)	$T_c(0)$ (K)	τ (h)	α	Error χ^2
0.79	28.69	14.43	61.3	0.5	0.243
0.79	**28.69**	**14.43**	**47.8**	**0.6**	**0.087**
0.79	28.69	14.43	40.8	0.7	0.150
0	13.03	21.11	4.09	0.5	0.023
0	**13.26**	**21.11**	**3.71**	**0.6**	**0.012**
0	13.41	21.11	3.48	0.7	0.048

gives the time-dependent changes in T_c which occur as the oxygen sublattice rearranges in response to the change in pressure. These two distinct contributions are seen in the inset to Fig. 3 where the application of 0.79 GPa pressure at 298 K (pt 1–2) causes a larger change in T_c than for the full release of this pressure at 53 K (pt 6–7). The reason for this result is that *some* relaxation occurs in YBCO at 298 K during the 17 min needed to apply the 0.79 GPa pressure followed by the 1/2 h anneal, but *none* occurs following the release of pressure at low temperatures, where $(dT_c/dP)_{\mathrm{OO}}=0$. From the latter data we then obtain using Eq. (1) $(dT_c/dP)_{\mathrm{intrinsic}}=dT_c/dP=(+1.95\pm0.05)$ K/GPa from data pts 6–7 in Fig. 3 or data pts 8–9 in Fig. 5. The data from pts 7–17 in Fig. 3, or pts 9–17 in Fig. 5(b), contain pure relaxation data at ambient pressure since the instantaneous change in T_c has already occurred.

The most direct way to obtain pure relaxation data for the sample at high pressures would be to apply the pressure at low temperatures, and then to anneal the sample at 298 K for different lengths of time. Unfortunately, the present pressure cell leaks if pressure is applied at low temperatures, so that pressure had to be applied at the annealing temperature 298 K itself. To account for the relaxation taking place during the pressure application we calculate[18] an additional time t_0 giving the equivalent time at the final pressure of 0.57 or 0.79 GPa which would give the same degree of relaxation. The value of t_0 obtained, $\sim$75 min in both cases, is then added to the nominal annealing times to obtain the data plotted in Figs. 4(a) and 5(a).

To obtain pure relaxation data at high pressures an additional correction is necessary: the initial value of $T_c(P,t=0)$ must be corrected for the ''intrinsic'' increase of T_c with pressure $(dT_c/dP)_{\mathrm{intrinsic}}=(+1.95\pm0.05)$ K/GPa. We account for this by simply adding this intrinsic shift at the appropriate pressure to the equilibrium T_c value at ambient pressure, i.e., 13.2 K, thereby obtaining the asterisk (*) data points in Figs. 3, 4(a), and 5(a).[19]

We are now in a position to analyze the pure relaxation data at 0, 0.57, and 0.79 GPa pressure. Since the third measurement series ''C'' is the most complete, including measurement times as long as 11 days, we discuss these data first. We analyze the relaxation behavior in terms of the stretched exponential[20,21]

$$T_c(t)=T_c(\infty)-[T_c(\infty)-T_c(0)]\exp\left\{-\left(\frac{t}{\tau}\right)^{\alpha}\right\}, \tag{2}$$

where $T_c(\infty)$ is the transition temperature after infinite time, $T_c(0)$ is the initial value of the transition temperature before relaxation has begun, τ is the relaxation time, and $\alpha\leqslant1$ is the stretched exponent.[22]

We now fit Eq. (2) to the experimental data in Fig. 5 (series C) using the relaxation time τ as a fit variable for fixed values of α. The best fits (solid lines) are obtained for $\tau=23.8$ h for the high-pressure data (0.57 GPa) and $\tau=11.1$ h for the ambient-pressure data with $\alpha=0.6$ in both cases. The best fits using other values of α are noticeably inferior (dashed lines). In Fig. 6 the data from Fig. 5(b) are fit using three different values of τ, each leading to a different value of $T_c(\infty)$. $\tau=11.1$ h gives the best fit. The values of all parameters used in these fits are listed in Table III. From the values for $T_c(0)$ and $T_c(\infty)$ we can now calculate the pressure derivative solely due to oxygen ordering: $(dT_c/dP)_{\mathrm{OO}}=+(18.05\pm0.05)$ K/GPa.

As already mentioned, the annealing times in measurement series B are too short to allow complete relaxation under pressure. In order to fit the data in Fig. 4 with reasonable parameters, $T_c(\infty)=28.68$ K is calculated for the pres-

TABLE III. Fit parameters for measurement series C used in Figs. 5 and 6. The optimal values are given in boldface type.

P (GPa)	$T_c(\infty)$ (K)	$T_c(0)$ (K)	τ (h)	α	Error χ^2
0.56	25.04	14.0	32.7	0.5	0.104
0.56	**24.29**	**14.0**	**23.8**	**0.6**	**0.032**
0.56	23.86	14.0	20.0	0.7	0.083
0	12.48	23.3	14.47	0.5	0.077
0	**13.13**	**23.3**	**11.10**	**0.6**	**0.009**
0	13.54	23.3	9.0	0.6	0.053
0	12.84	23.3	13.0	0.6	0.032
0	13.45	23.3	9.77	0.7	0.041

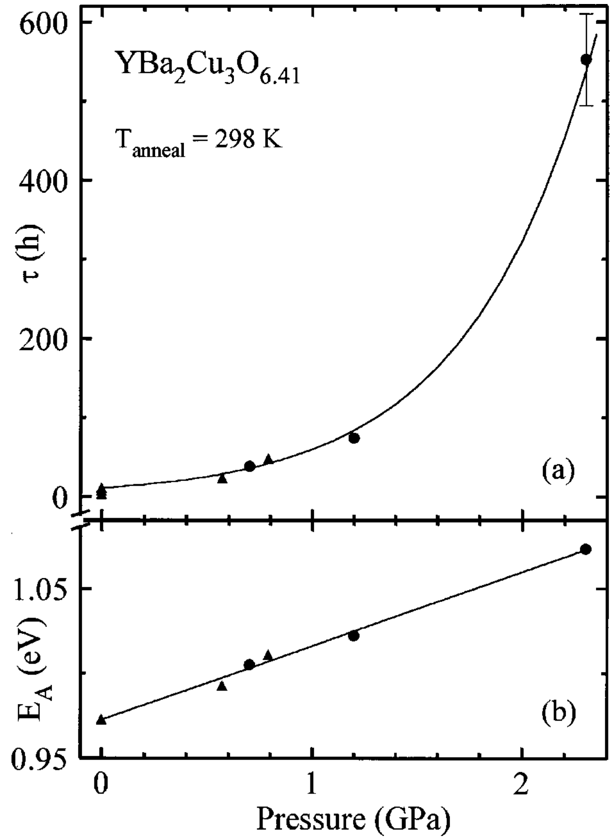

FIG. 7. (a) Pressure dependence of the relaxation time τ obtained from the data fits in Figs. 2, 4, 5, and 6 (solid triangles, ▲) and from the diamond-anvil-cell experiments in Ref. 24 (solid circles, ●). Except at 2.3 GPa, the error is less than the size of the symbols. Relaxation processes slow down markedly under pressure. (b) Pressure dependence of the activation energy E_A. The slope of the linear fit (solid line) is used to calculate the activation volume (see text).

sure of 0.79 GPa based on $(dT_c/dP)_{\mathrm{OO}} = +18.05$ K/GPa from measurement series C. $T_c(\infty)$ is then also used as a fixed value for the fit which yields $\tau = 47.8$ h and $\alpha = 0.6$. Ambient pressure data from series A and C could be best fit with $\alpha = 0.6$ as well.

The values of all parameters used in the above fits are listed in Tables I–III. The ''best-fit'' relaxation times τ are seen in Fig. 7 (solid triangles) to increase rapidly with increasing pressure from ~ 10 to 50 h, a fact which is already apparent upon visual inspection of the relaxation data in Figs. 4 and 5. There is some spread in the values of τ in the three measurement series A, B, and C at ambient pressure. This is most likely due to the fact that relaxation under pressure was not complete for measurement series A and B, resulting in different starting conditions for the relaxation measurements at 0 GPa after pressure release. Longer relaxation times were obtained for more complete relaxation under pressure.

In a separate experiment to higher pressures, a small piece taken from the YBCO sample used in the present study was placed in a diamond-anvil cell loaded with dense He in which the superconducting transition could be detected via the ac susceptibility.[23] Three measurement series at 0.7, 1.2, and 2.3 GPa were carried out and analyzed in the same manner as above, yielding the relaxation times and activation energies shown in Fig. 7 as solid circles. The results of this experiment in the diamond-anvil cell will be discussed in detail elsewhere.[24]

V. DISCUSSION

A. Relaxation at low temperatures

Although the present experiments give no evidence for oxygen relaxation phenomena in the temperature range 14–250 K, we cannot rule out the possibility that relaxation occurs at temperatures below 14 K. We can, however, place an upper limit on the activation energy for such processes. Since no change in T_c is observed for annealing temperatures between 14 and 250 K, very low-temperature relaxation, if present, must be complete after the 10 min time required for the release of pressure at 14 K, i.e., $\tau(14\,\mathrm{K}) \leq 10$ min at ambient pressure. Assuming an Arrhenius law for the relation between activation energy and relaxation time

$$\tau = \tau_0 \cdot \exp\left\{\frac{E_A}{k_B T}\right\}, \qquad (3)$$

and the attempt period $\tau_0 \approx 1.4 \times 10^{-12}$ s from quench experiments,[2] we estimate $E_A \leq 0.040$ eV at ambient pressure. For the pressure 0.79 GPa, the limit $E_A \leq 0.152$ eV is calculated.

The upper limit for the activation energy of this hypothetical very low-temperature relaxation process at ambient pressure, $E_A \leq 0.040$ eV, is less than the values of E_A (0.08, 0.12, and 0.18 eV) obtained in internal friction measurements.[10] There are at least two possible explanations for the presence of relaxation peaks at low temperatures in the internal friction studies, but the absence of low-temperature relaxation above 14 K in the present experiments: (i) the atomic motion detected in the internal friction studies may be of a kind that causes no change in the transition temperature T_c—this would be the case, for example, if ions other than oxygen are involved or if the oxygen motion is between on-chain and off-chain sites in the basal plane which does not change the valence of Cu(1), so that no charge is transferred and T_c remains unaffected, and (ii) the polycrystalline sample used in the internal friction studies may have loss modes associated with grain boundaries which are not present in our single-crystalline sample.

B. Pressure-dependent oxygen relaxation

Whereas the stretched exponential $\alpha = 0.5$ was used in previous studies,[2,25] our relaxation data are best fit for $\alpha = 0.6$. The precise physical meaning of the exponent α is still a matter of controversy.[20,21] Most models propose a distribution of activation energies E_A rather than a single activation energy where one would expect $\alpha = 1$. A distribution of activation energies in the Arrhenius law [Eq. (3)] results in an exponent $\alpha < 1$ in the exponential time dependence in Eq. (2). The hierarchical model[20] proposes distinct interdependent diffusion processes which take place after one another, later processes only being possible after earlier ones have taken place. Another model[21] accounts for the stretched exponential by a distribution of activation energies belonging to different processes occurring at the same time parallel to each other. Based on the present results neither of the models can be favored or ruled out.

The ambient pressure value of $E_A=(0.97\pm0.01)$ eV obtained in the present analysis is in good agreement with the values obtained from both thermal disorder[2,25] and tracer diffusion studies.[7] In Fig. 7 it is seen that the relaxation time τ increases in a superlinear manner under pressure, whereas the activation energy increases approximately linearly (the attempt period $\tau_0\simeq1.4\times10^{-12}$ s is assumed to be pressure independent). The straight line in Fig. 7(b) represents the best fit to all data up to 2.3 GPa, yielding $dE_A/dP\simeq+(44\pm2)$ meV/GPa. If only the He-gas data (solid triangles) are fit, the pressure dependence changes only slightly to $dE_A/dP\simeq+(46\pm10)$ meV/GPa. It is thus evident that diffusion processes in YBCO slow down markedly under pressure. From our results we estimate the relaxation time at 5 GPa to be 6.5 years. This pressure-dependent relaxation must be taken into account when analyzing $T_c(P)$ data on YBCO to very high pressures. Dyakonov *et al.*[26] have very recently reported that in $NdBa_2Cu_3O_{6.67}$ the oxygen ordering processes appear to slow down under pressure.

The relaxation time τ in YBCO has recently been found to increase with decreasing oxygen content.[6] Since both the unit-cell volume and the area of the basal plane in YBCO increases with decreasing oxygen content,[1] this increase in τ would not appear to be related to the present result where τ increases under pressure (decreasing unit-cell volume). The increase in τ with decreasing oxygen content might be related to the fact that at lower oxygen concentrations the oxygen ordering process involves the diffusion of oxygen anions over larger distances in the sparcely populated oxygen sublattice.

The pressure dependence of diffusion phenomena is normally analyzed in terms of the activation volume ΔV_A which can be calculated from the pressure dependence of the relaxation time[27]

$$\Delta V_A=\Delta V_f+\Delta V_m=RT\left(\frac{\partial \ln\tau}{\partial P}\right), \tag{4}$$

where ΔV_f is the change in volume due to the formation of a vacancy or interstitial, and ΔV_m is the volume change due to the migration of the diffusing atom. The activation volume obtained from Eq. (4) for the present RT data is positive in sign and given by $\Delta V_A=(4.2\pm0.2)$ cm^3/mol. This molar volume is 73% of that (5.78 cm^3/mol) of the diffusing species, the oxygen O^{2-} ion in the CuO chain layer. In the present case we can assume that $\Delta V_f=0$, since the oxygen vacancies are already present and need not be created. Thus, the activation volume determined represents only the migration volume. A positive sign for the activation volume of migration is found for the majority of metals and ionic compounds.[28]

In a different approach, Theiss *et al.*[29] determined the activation volume for interdiffusion in SiGe amorphous thin films by scaling the time axis of the pressure-dependent diffusion data, so that data points for different pressures fall on the same curve. The scaling factor γ is a function of pressure and its logarithmic pressure derivative leads to the activation volume. The advantage of this method of analysis is its independence from any fit equation like Eq. (2). This alternate analysis of our data gives within 3% the same value of ΔV_A as obtained above.

In summary, the present studies under high pressure on an oxygen-deficient YBCO crystal have given no evidence for relaxation processes in the oxygen sublattice at low temperatures (14–250 K), in contrast to the relaxation behavior in Tl-2201. The relaxation peaks observed in internal friction studies on YBCO at low temperatures thus apparently involve processes with no link to the superconducting state. We do observe relaxation in T_c for temperatures above 250 K, yielding a distribution of activation energies near 0.97 eV, in agreement with earlier high-pressure studies and tracer diffusion measurements. We find the relaxation time to increase rapidly with pressure from approximately 10 h at ambient pressure to 50 h at 0.79 GPa and to 550 h at 2.3 GPa; the corresponding rate of increase of the activation energy is $dE_A/dP\simeq+44$ meV/GPa.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. DMR 95-09885. Work at Argonne was supported by the U.S. Department of Energy, Division of Basic Energy Sciences, under Contract No. W-31-109-ENG-38 (B.V., A.P.) and by the National Science Foundation, Science and Technology Center for Superconductivity under Contract No. DMR 91-2000 (H.Z.).

---

[1] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature (London) **329**, 423 (1987); Phys. Rev. B **36**, 5719 (1987).

[2] B. W. Veal, A. P. Paulikas, H. You, H. Shi, Y. Fang, and J. W. Downey, Phys. Rev. B **42**, 6305 (1990).

[3] B. W. Veal and A. P. Paulikas, Physica C **184**, 321 (1991).

[4] R. Sieburger and J. S. Schilling, Physica C **173**, 423 (1991).

[5] W. H. Fietz, J. Metzger, T. Weber, K. Grube, and H. A. Ludwig, in *High-Pressure Science and Technology*, Colorado Springs, 1993, edited by S. C. Schmidt *et al.*, AIP Conf. Proc. No. 309 (AIP, New York, 1993), p. 703.

[6] W. H. Fietz, R. Quenzel, H. A. Ludwig, K. Grube, S. I. Schlachter, F. W. Hornung, T. Wolf, A. Erb, G. Müller-Vogt, and M. Kläser, Physica C **270**, 258 (1996).

[7] S. J. Rothman, J. L. Routbort, and J. E. Baker, Phys. Rev. B **40**, 8852 (1989).

[8] A.-K. Klehe, C. Looney, J. S. Schilling, H. Takahashi, N. Môri, Y. Shimakawa, Y. Kubo, T. Manako, S. Doyle, and A. M. Hermann, Physica C **257**, 105 (1996).

[9] C. Looney, J. S. Schilling, S. Doyle, and A. M. Hermann, Physica C (to be published).

[10] M. Weller, Mater. Sci. Forum **119-121**, 667 (1991).

[11] J. Guimpel, B. Maiorov, E. Osquiguil, G. Nieva, and F. Pardo, Phys. Rev. B **56**, 3552 (1997).

[12] J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W.

Crabtree, H. Claus, and W. K. Kwok, Phys. Rev. B **41**, 1863 (1990).

[13] I. L. Spain and S. Segall, Cryogenics **11**, 26 (1971).

[14] V. V. Fufaev, Electrotekhnika **65**, 52 (1994) [Russ. Electr. Eng. **65**, 83 (1994)].

[15] H. Takahashi, A.-K. Klehe, C. Looney, J. S. Schilling, N. Môri, Y. Shimakawa, Y. Kubo, and T. Manako, Physica C **217**, 163 (1993); J. S. Schilling, J. Diederichs, S. Klotz, and R. Sieburger, in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, edited by R. A. Hein, T. L. Francavilla, and D. H. Liebenberg (Plenum, New York, 1991), p. 107.

[16] From Fig. 1 $\Delta\chi \simeq (-37\times 19^{-3}$ emu/g$)\rho = 0.237$ emu/cm^3 using the density of YBCO, $\rho = 6.4$ g/cm^3; for ideal diamagnetism $\Delta\chi = (-1/4\pi)(1-\mathcal{D})^{-1} = 0.237$ emu/cm^3, implying $\mathcal{D} = 0.66$.

[17] The 17 h anneal at 298 K was dictated by the fact that the relaxation time for oxygen ordering in samples with similar oxygen content is reportedly 6–8 h (see Ref. 6).

[18] In order to make this estimate of t_0, the data were first fit using Eq. (2) assuming $t_0 = 0$. The obtained relaxation times ($\tau = 27.0$ h and 49.7 h for 0.57 GPa and 0.79 GPa, respectively) were then used to estimate the equivalent time t_0 at high pressure from the time spent to apply pressure, yielding $t_0 = 75$ min for both pressures. This time is then added to all annealing times. The relaxation times now obtained from a fit using Eq. (2), 23.8 h for 0.57 GPa and 47.8 h for 0.79 GPa, differ only slightly from the values obtained above assuming $t_0 = 0$.

[19] Pressure changes due to the contraction of helium with decreasing temperature have been taken into account in these calculations.

[20] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[21] D. Redfield, in *Amorphous Silicon Technology-1992*, edited by M. J. Thompson *et al.*, MRS Symposia Proceedings No. 258 (Materials Research Society, Pittsburgh, 1992), pp. 341–346.

[22] For relaxation processes with a single relaxation energy, the exponent α is equal to one $(\alpha = 1)$. In this case, the value of τ obtained from a fit to the data using Eq. (2) is independent of which data point is chosen to represent the initial data point $T_c(0)$. However, for a distribution of relaxation times, where $\alpha < 1$, it is essential that the complete set of relaxation data are used; this is the reason we take care to accurately determine the equivalent relaxation time t_o during the application of pressure.

[23] For a description of our diamond-anvil-cell measurement techniques, see Ref. 9 and: J. S. Schilling, J. Diederichs, S. Klotz, and R. Sieburger, in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, edited by R. A. Hein, T. L. Francavilla, and D. H. Liebenberg (Plenum, New York, 1991), p. 107; S. Klotz, J. S. Schilling, and P. Muller, in *Frontiers of High-Pressure Research*, edited by H. D. Hochheimer and E. D. Etters (Plenum, New York, 1991), p. 473.

[24] V. Tissen, Y. Wang, and J. S. Schilling (unpublished).

[25] J. D. Jorgensen, Shi Hao, A. P. Paulikas, B. W. Veal, Pei Shiyou, and P. Lightfoot, Physica C **167**, 571 (1990).

[26] V. Dyakonov, I. Fita, N. Doroshenko, M. Baran, S. Piechota, and H. Szymczak, Physica C **276**, 245 (1997).

[27] G. W. Tichelaar and D. Lazarus, Phys. Rev. **113**, 438 (1959).

[28] D. Lazarus and N. H. Nachtrieb, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963), and references therein.

[29] S. D. Theiss, F. Spaepen, and M. J. Aziz, Appl. Phys. Lett. **68**, 1226 (1996).