Relaxation effects in the transition temperature of superconducting HgBa$_2$CuO$_{4+\delta}$

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Abstract

In previous studies on a number of under- and overdoped high temperature superconductors, including YBa$_2$Cu$_3$O$_{7-y}$ and Tl$_2$Ba$_2$CuO$_{6+\delta}$, the transition temperature $T_c$ has been found to change with time in a manner which depends on the sample’s detailed temperature and pressure history. This relaxation behavior in $T_c$ is believed to originate from rearrangements within the oxygen sublattice. In the present high-pressure studies on HgBa$_2$CuO$_{4+\delta}$ to 0.8 GPa we find clear evidence for weak relaxation effects in strongly under- and overdoped samples ($T_c \simeq 40 - 50$ K) with an activation energy $E_A(1$ bar) $\simeq 0.8 - 0.9$ eV. For overdoped HgBa$_2$CuO$_{4+\delta}$ $E_A$ increases under pressure more rapidly than previously observed for YBa$_2$Cu$_3$O$_{6.41}$, yielding an activation volume of $+11 \pm 5$ cm$^3$; the dependence of $T_c$ on pressure is markedly nonlinear, an anomalous result for high-$T_c$ superconductors in the present pressure range, giving evidence for a change in the electronic and/or structural properties near 0.4 GPa.
I. INTRODUCTION

The study of the mercury-oxide family \( \text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \) is of particular interest since these cuprates possess the highest transition temperatures \( T_c \) of all known high-temperature superconductors (HTSC). For the Hg-compound containing one CuO\(_2\)-layer, \( \text{HgBa}_2\text{CuO}_{4+\delta} \) (Hg-1201), \( T_c \) reaches values as high as 98 K at ambient pressure \(^1\) and can reportedly be varied over the entire range from extreme under- to overdoped solely by changing the oxygen content \(^3\). The Hg-compound containing three CuO\(_2\)-layers exhibits the highest ambient-pressure transition temperature \( (T_c \simeq 134 \text{ K}) \) reported to date, increasing to \( T_c \approx 164 \text{ K} \) under 30 GPa pressure \(^4\).

High-pressure experiments are potentially an important tool to further our understanding of the superconducting state \(^3\)\(^4\). For the Hg-compounds the dependence of \( T_c \) on pressure was first studied by Klehe et al. \(^2\) on optimally doped Hg-1201 where \( T_c \) was found to increase linearly with hydrostatic pressure to 1 GPa at the rate + 1.75 K/GPa. An identical initial pressure dependence was subsequently observed by Klehe et al. \(^8\) for the two- and three-layer compounds \( \text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta} \) (Hg-1212) and \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta} \) (Hg-1223); this parallelism in the \( T_c(P) \)-dependence for all three optimally doped Hg-compounds was later confirmed to much higher pressures \((>30 \text{ GPa})\) by Gao et al. \(^4\) who observed that \( T_c \) initially increases, but passes through a maximum and decreases at higher pressure. In fact, for the majority of HTSC compounds near optimal doping, \( T_c(P) \) is found to follow a similar bell-shaped curve \(^3\)^{5\(^\text{•}\)^\text{•}}\(^\text{•}\).

Cao et al. \(^10\) studied the pressure dependence of \( T_c \) for Hg-1201 to 1.5 GPa at widely differing doping levels by varying the oxygen concentration; Qiu et al. \(^1\) extended these studies to 18 GPa for selected samples with \( T_c \) values at or above 80 K. Jansen and Block \(^12\) have attempted a quantitative analysis of these experiments using an indirect-exchange pairing mechanism between conduction electrons via oxygen anions; the doped oxygen thus fulfills a dual role as both hole dopant and Cooper pair mediator. In this model calculation pressure effects on \( T_c \) are assumed to originate solely from a change in unit cell volume;
possible rearrangements of oxygen defects within the unit cell when pressure is applied are not considered.

Before attempting to gain information about the superconducting state from a detailed analysis of $T_c(P)$-data on the superconducting oxides, it is essential to know, on a microscopic scale, what structural changes actually occur under pressure. It would be hoped that $T_c(P)$ is indeed a reversible, single-valued function of pressure, as in conventional superconductors. This has appeared to be the case in the vast majority of experiments on the superconducting oxides where the pressure was changed at ambient temperature. Surprisingly, experiments carried out by Sieburger et al. [13] on Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2201) revealed that the initial dependence of $T_c$ on pressure can change by an order of magnitude, depending on the temperature at which the pressure is varied; even the sign of $dT_c/dP$ may change. $T_c(P)$ is thus not a unique function of pressure but depends strongly on the detailed temperature-pressure history of the sample. Because this anomalous behavior is a sensitive function of the concentration of interstitial oxygen $\delta$ in Tl-2201, it has been attributed [13] to relaxation effects within the oxygen sublattice; indeed, evidence for strong relaxation effects in $T_c$ from oxygen ordering were first obtained by Veal et al. [14] in temperature-quench experiments on strongly underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123). Evidence for relaxation effects in Y-123 from high-pressure data was obtained somewhat later [15,16].

In the meantime many oxide superconductors have been found which exhibit pressure-induced relaxation effects [3], including TlSr$_2$CaCu$_2$O$_{7-\delta}$ (Tl-1212) [17], Nd-123 [18], Gd-123 [19], superoxygerated La$_2$CuO$_{4+y}$ [20], and possibly Sr$_2$CuO$_2$F$_{2+y}$ [21]. For all these systems, except Tl-2201, relaxation effects become activated for temperatures above 200 K. In Tl-2201 two distinct relaxation processes are activated in the temperature ranges 15 - 100 K and 200 - 300 K, respectively [22,23]. In view of the importance of relaxation phenomena in many high-$T_c$ superconductors, it would be of interest, before carrying out detailed comparisons between theory and experiment, to determine whether or not they play a role in the Hg-oxide system where the values of $T_c(P)$ are relatively high, and, at least in Hg-1201, the oxygen defect structure is known to be quite complex [24]. In Hg-1212 and
Hg-1223 evidence for oxygen ordering along the c-axis has been obtained in energy dispersive synchrotron X-ray diffraction experiments for pressures above $\sim 15$ GPa \cite{25}; the effect of this ordering on $T_c$ was not studied.

In this paper we show evidence for the existence of weak pressure-induced relaxation effects in $T_c$ for both under- and overdoped Hg-1201 which are activated at temperatures above 200 K. Previous $T_c(P)$ studies by us on optimally doped Hg-1201 \cite{3} gave no evidence for relaxation behavior. In the overdoped Hg-1201 samples the pressure dependence $T_c(P)$ to 0.8 GPa is clearly nonlinear, providing evidence for a possible pressure-induced electronic and/or structural modification.

II. EXPERIMENT

In the present experiments one underdoped sample and two overdoped samples (A and B) of polycrystalline HgBa$_2$CuO$_{4+\delta}$ with transition temperatures in the range 40 - 50 K were studied. Typical sample sizes were 2×1×1 mm$^3$ with masses ranging from 4 to 12 mg. All samples were synthesized in an evacuated quartz tube as described previously \cite{26}. Both the single underdoped sample and the overdoped sample A were obtained from a single synthesis by subsequent annealing to produce samples with significantly different oxygen contents but similar values of $T_c$. The overdoped sample A ($T_c$(1 bar) $\simeq$ 47.81 K) was annealed in 150 atm. oxygen at 220°C for 100 h followed by a slow cool to room temperature, whereas the underdoped sample ($T_c$(1 bar) $\simeq$ 47.55 K) was annealed in flowing argon at 400°C for 24 h and then rapidly cooled to room temperature. The overdoped sample B ($T_c$(1 bar) $\simeq$ 40.0 K) was obtained from a second synthesis in powder form and annealed in 30 atm. oxygen at 200°C for 100 h. Neutron diffraction experiments on these samples determined the oxygen contents at $x \approx 0.22$ \cite{27} and 0.12 \cite{24} for the overdoped sample A and the underdoped sample, respectively.

The He-gas pressure system (Harwood) used in this study is capable of generating 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 cell can be changed at any temperature above the melting curve $T_m$ of the He pressure medium [28] (for example, $T_m \simeq 13.8$ K at 0.1 GPa and $T_m \simeq 52.4$ K at 0.8 GPa). The decrease in pressure upon cooling is kept to below 20% by the introduction of a sizeable room temperature “dead volume”. Unless otherwise stated, the value of the pressure given was determined at a temperature near $T_c$.

The superconducting transition of the Hg-1201 samples is measured by the ac susceptibility technique using a miniature primary/secondary coil system located inside the 7 mm I.D. bore of the pressure cell. In the present studies a magnetic field of 1.1 Oe (rms) at 507 Hz is applied along the long dimension of the sample. Further details of the experimental setup are given elsewhere [29].

### III. RESULTS OF EXPERIMENT

#### A. Overdoped Sample

Fig. 1 shows the transition to superconductivity for the overdoped Hg-1201 sample A at ambient pressure. The transition is measured by sweeping through the temperature range 10 K to 55 K over a 2 h period, yielding the value $T_c(1$ bar) $\simeq 47.81$ K (inset in Fig. 1) for the superconducting onset. The size of the transition corresponds to full shielding, if the demagnetization factor $D$ is neglected [30]. The transition temperature in the subsequent measurements under high pressure is determined by shifting the upper 15% of the full transition along the temperature axis until overlap is achieved with the initial measurement. Only the upper portion of the transition is used because this region is independent of the applied magnetic field. Through this procedure an accuracy of ± 20 mK for the relative $T_c$ shifts under pressure could be achieved. In most experiments the transition was remeasured for verification.

The first set of high-pressure data for the overdoped Hg-1201 sample A (open circles in
Fig. 2a) was taken by applying 0.16 GPa at 298 K and holding this pressure for one hour, followed by a rapid cooldown (3 - 4 K/min) to measure \( T_c \). At temperatures near \( T_c \) the measured pressure had decreased to 0.12 GPa due to the thermal contraction of the helium pressure medium upon cooling. The sample was then heated back to 298 K, the pressure increased and \( T_c \) remeasured. This procedure was repeated up to the highest pressure of 0.61 GPa (0.54 GPa at 50 K). The pressure dependence \( T_c(P) \) is seen to be markedly nonlinear, an anomalous result in this pressure range for high-\( T_c \) oxides.

The second set of data on this sample (solid squares in Fig. 2a) was taken by applying 0.79 GPa at 298 K (0.71 GPa at 50 K) followed by a one hour anneal at this temperature. After measuring \( T_c \) and heating back up to 298 K, the pressure was decreased by \( \sim 20\% \), held for one hour at 298 K, and \( T_c \) remeasured. This procedure was then repeated several times until the pressure was fully released; \( T_c \) is seen to return to its initial value at 47.8 K. For pressure changes at room temperature (RT), \( T_c(P) \) thus appears to be a reversible, but markedly nonlinear, function of pressure with initial slope \( (dT_c/dP)_{RT} \approx -1.55 \pm 0.26 \) K/GPa.

We now determine the hydrostatic pressure dependence of \( T_c \) for pressure changes at low temperatures, an experiment that can best be carried out using a He-gas high-pressure system. In the third set of data on the overdoped sample A (solid diamonds in Fig. 2a), we first apply and hold 0.76 GPa pressure at 298 K for 10 min before cooling down rapidly to measure \( T_c \) \( (P = 0.69 \) GPa at 50 K). Some pressure was then added at 60 K to obtain 0.75 GPa and \( T_c \) was remeasured. The pressure was then successively decreased at low temperatures \( (T < 55 \) K) and \( T_c \) redetermined. The value of \( T_c \) at ambient pressure is now seen to lie 0.26 K below its initial value. Only after annealing the sample at 298 K for 40 min does \( T_c \) shift back to its initial value (47.81 K) within the experimental accuracy of \( \pm 0.02 \) K. These data demonstrate that the pressure dependence of \( T_c \) is clearly nonlinear. The fact that \( T_c(P) \) depends on the temperature at which the pressure is changed gives evidence for relaxation behavior in overdoped Hg-1201, as discussed in the Introduction; the time dependence of this relaxation will be examined below. From Fig. 2a the initial slope
near 1 bar for pressure changes at low temperature is $(dT_c/dP)_{LT} ≃ -1.15 \pm 0.52 \text{ K/GPa}$.

To establish whether the above nonlinearity in $T_c(P)$ is an accidental occurrence or is characteristic for overdoped Hg-1201 samples, a second overdoped sample (B) with $T_c ≃ 40.0 \text{ K}$ from a different synthesis was studied. As seen in Fig. 2b, pressure was applied successively at 298 K (open circles) and released in steps (closed circles) at low temperature (<65 K). This procedure was then repeated (open and closed triangles) to check the reproducibility of the data. Evidence for nonlinearity in $T_c(P)$ is also seen in Fig. 2b for this sample; however, the pressure above which the change in slope occurs appears to be shifted to higher pressures for sample B ($\sim 0.5 \text{ GPa}$) relative to sample A ($\sim 0.4 \text{ GPa}$). For sample B we find the initial slopes $(dT_c/dP)_{RT} ≃ -0.66 \pm 0.18 \text{ K/GPa}$ and $(dT_c/dP)_{LT} ≃ -0.57 \pm 0.30 \text{ K/GPa}$ which have approximately half the magnitude of those for the less strongly overdoped sample A. The magnitude and even the sign of $(dT_c/dP)_{RT}$ differ from the results of Cao et al. [10] on similarly overdoped Hg-1201; the reason for this discrepancy is unknown, but may arise from differences in the pressure medium (He versus Flourinert), pressure technique, details of sample preparation or measurement technique (ac susceptibility versus resistivity). Interestingly, the data of Cao et al. [10] for strongly overdoped Hg-1201 reveal a nonlinearity in $T_c(P)$ near 0.5 GPa, but the sign of the change in slope $dT_c/dP$ is opposite to ours.

We would now like to determine the temperature at which the relaxation behavior in the overdoped Hg-1201 sample A initiates. The sample studied (second piece from the same pellet) exhibited $T_c ≃ 47.62 \text{ K}$ at ambient pressure (pt. 1 in Fig. 3). Applying and holding 0.67 GPa pressure at 298 K for 1 h, $T_c$ decreased to pt. 2 (47.18 K). Immediately following the $T_c$ measurement, the pressure was fully released at 50 K, yielding $T_c ≃ 47.32 \text{ K}$ (pt. 3 in Fig. 3), which lies 0.3 K lower than the initial value at ambient pressure. The value of $T_c$ is found not to change following anneals for 1 h at 100 K (pt. 4) and then for another hour at 200 K (pt. 5). However, $T_c$ is seen to relax back toward its initial value following 1 h (pt. 6) and then 3 h (pt. 7) anneals at 298 K. The data in Fig. 3 thus show that relaxation effects are only activated for temperatures above 200 K. We cannot exclude the possibility
that relaxation phenomena occur at temperatures below 50 K since in the present studies the measurement of $T_c$ itself constitutes annealing the sample at $\sim 50$ K.

We now examine the time-dependence of the relaxation phenomena for overdoped Hg-1201 at three different pressures. In these measurements a third piece of sample A was studied with $T_c \simeq 47.81$ K at ambient pressure; full shielding was exhibited [30]. A pressure of 0.61 GPa was applied and held 1 h at 298 K before cooling to measure $T_c \simeq 47.38$ K. After the full release of pressure at 48 K, we find $T_c \simeq 47.58$ K (pt. 1 in Fig. 4a). The sample was then heated to 265 K and held for 1 h, before cooling rapidly to measure $T_c \simeq 47.64$ K (pt. 2 in Fig. 4a). Subsequent annealing at 265 K for longer times gives the $T_c$ values represented by points 3 to 7 in Fig. 4a. The fit to the data, which yields a relaxation time $\tau \simeq 3.4$ h, is discussed below. The difference of 70 mK between the value of $T_c$ at the outset of the experiment (47.81 K) and the final value (47.74 K) is likely due to the different annealing temperature (here $T_a = 265$ K versus 298 K for the initial measurement). We previously observed a similar effect in YBa$_2$Cu$_3$O$_{6.41}$ [14,31]. As we discuss in more detail below, a lower annealing temperature leads to a higher state of oxygen order which increases the hole-carrier concentration in the CuO$_2$ planes, shifting $T_c$ up for an underdoped sample or down for an overdoped sample, as observed.

Our previous studies on YBa$_2$Cu$_3$O$_{6.41}$ [31] revealed that the relaxation behavior itself is strongly pressure dependent. To address this question for the present overdoped Hg-1201 sample A, a pressure of 0.62 GPa was applied and held at 298 K for 1 h. Following the partial release of pressure to 0.13 GPa at 53 K, $T_c$ was found to be 47.41 K (pt. 1 in Fig. 4b). Subsequent annealing at $T_a \simeq 265$ K (P $\simeq 0.15$ GPa at this temperature) for various time periods up to a total of 145 h gives the relaxation behavior represented by points 2 to 8 in Fig. 4b. A cursory comparison of the data in Figs. 4a and 4b reveals that the relaxation time $\tau(265$ K) has become longer under pressure. To determine $\tau$ at higher pressures, the sample was then subjected to 0.7 GPa pressure at 298 K for 1.6 h which was then partially released to 0.25 GPa at 52 K (pt. 1 in Fig. 4c). Because of the rapid increase in $\tau$ with pressure, the annealing temperature was increased to 285 K to speed up the relaxation. The
sample was annealed up to a total time of 42.5 h (pts. 2 to 6 in Fig. 4c).

We now analyze the time-dependent relaxation behavior of $T_c$ in Fig. 4 in terms of the stretched exponential \[ T_c(t)_{\text{relax}} = T_c(\infty) - [T_c(\infty) - T_c(0)] \exp \left\{ -\left( \frac{t}{\tau} \right)^\alpha \right\}, \] (1)
where $T_c(\infty)$ is the transition temperature at a given pressure after infinite time, $T_c(0)$ is the initial value of the transition temperature at a given pressure before relaxation begins, $\tau$ is the temperature- and pressure-dependent relaxation time, and $\alpha \leq 1$ is the stretched exponent. In a previous analysis of relaxation behavior on a strongly underdoped Y-123 single crystal \[31\], where the pressure-induced shifts in $T_c$ were large and the data could be analyzed to high accuracy, we found $\alpha = 0.6$, independent of the pressure. For the present overdoped Hg-1201 compound the measured shifts in $T_c$ are much smaller, resulting in relatively large error bars. In the following we use $\alpha = 0.6$ \[34\] and set the transition temperature at zero time, $T_c(0)$, to the value measured immediately after the pressure release at low temperatures, before any relaxation could take place.

A fit with Eq. (1) to the ambient-pressure relaxation data at 265 K in Fig. 4a (solid line) is seen to describe the data well within experimental error, yielding the parameters $T_c(\infty) \simeq (47.74 \pm 0.01)$ K and $\tau(265 \text{ K}) \simeq (3.4 \pm 0.6)$ h. A second experiment (not shown) under similar conditions gives $\tau(265 \text{ K}) \simeq (3.9 \pm 0.7)$ h, in agreement with the previous value. A fit to the relaxation data at 0.15 GPa and 265 K in Fig. 4b yields $T_c(\infty) \simeq (47.55 \pm 0.01)$ K and $\tau(265 \text{ K}) \simeq (17.5 \pm 5.4)$ h. This relaxation time is distinctively longer than the ambient pressure values, implying that the relaxation slows down rapidly under pressure. Since the relaxation at 0.30 GPa and 285 K in Fig. 4c proceeded somewhat more rapidly than anticipated, a small correction to the annealing time is necessary to account for the finite time spent warming(cooling) the sample to(from) the annealing temperature. Based on the relaxation time obtained from a preliminary fit to the data with Eq. (1), we estimate that this correction amounts to only $\sim 4$ min. The corrected data in Fig. 4c are now fit with Eq. (1), yielding $T_c(\infty) \simeq (47.46 \pm 0.01)$ K and a relaxation time $\tau(285 \text{ K}) \simeq (0.92 \pm 0.10)$
B. Underdoped Sample

We now study the pressure dependence of $T_c$ on an underdoped Hg-1201 sample with $T_c(1 \text{ bar}) \simeq 47.55 \text{ K}$, an almost identical value to that for the overdoped sample A. Since the superconducting onset is less sharp than that for the overdoped sample, changes in $T_c$ under pressure cannot be determined as accurately ($\pm 50 \text{ mK}$ versus $\pm 20 \text{ mK}$). Following the initial measurement of $T_c$ at ambient pressure (pt. 1 in Fig. 5), a pressure of 0.79 GPa was applied at 298 K and held for 15 minutes before cooling down to measure $T_c \simeq 48.55 \text{ K}$ (pt. 2 in Fig. 5); the pressure at this temperature was 0.71 GPa, yielding the pressure derivative $(dT_c/dP)_{RT} \simeq +1.41 \pm 0.14 \text{ K/GPa}$, a value somewhat less than that ($+2 \text{ K/GPa}$) reported for underdoped Hg-1201 by Cao et al. [10]. Pressure was then successively decreased at temperatures below 90 K and $T_c$ immediately remeasured each time (pts. 3 to 9 in Fig. 5), revealing a linear dependence of $T_c$ on pressure $(dT_c/dP)_{LT} \simeq +1.15 \pm 0.05 \text{ K/GPa}$. After the pressure was released (pt. 9), $T_c$ was found to lie 150 mK higher than the initial value (pt. 1). Annealing the sample at 298 K for a total of 4 h (pts. 10 - 12) fully restored the initial $T_c$ value.

Annealing this sample for extended time periods at RT apparently causes some sample degradation, as evidenced by irreversible changes in the shape of the superconducting transition. A strong degradation of underdoped Hg-1201 samples stored in air was recently reported by Peacock et al. [35] in which $T_c$ increased from 30 K to 75 K over the time span of 6.5 weeks following their synthesis. This gradual shape change in the transition and the smallness of the relaxation effect itself precluded a detailed measurement of the time, temperature and pressure dependence of the relaxation phenomena for this underdoped sample; from the data, however, we can give a rough estimate of the relaxation time at ambient pressure, namely $\tau(298 \text{ K}) \approx 1 \text{ h}$. 

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IV. DISCUSSION

A. Intrinsic Pressure Dependence of $T_c$

Pressure-induced relaxation effects have been observed in several high-$T_c$ superconductors, including Y-123, Tl-2201 and Tl-1212 [6]. Very recent studies on underdoped Y-123 have shown that $T_c(P)$ to 17 GPa depends markedly on whether the pressure is applied at ambient or low temperatures [36–38]. In oxide superconductors, therefore, the measured dependence of $T_c$ on pressure may depend in a sensitive manner on the detailed pressure/thermal history of the sample. The high pressure environment does not create the relaxation processes, but rather makes those already present under ambient conditions more readily visible than in conventional temperature-quench experiments.

Theoretical calculations of the properties of matter, including their superconductivity, are generally carried out for a given fixed set of lattice parameters and atomic coordinates; pressure effects are generally estimated under the assumption that the change in properties, like $T_c$, is a function of the anisotropic decrease in the lattice parameters, with all atomic separations scaling accordingly. Before a measured $T_c(P)$-dependence can be compared in a quantitative way with theory, therefore, it should be purified of all influences from relaxation behavior. Since most high-pressure cells only allow the pressure to be changed at room temperature, many results from the large body of high-pressure studies on high-$T_c$ materials do contain relaxation effects and thus must be repeated using high-pressure technology similar to ours to separate intrinsic from relaxation effects.

In the oxide superconductors the measured value of the transition temperature $T_{c, meas}(\delta, P, T_a, t)$ is a function of both the doping level $\delta$ and the sample’s detailed pressure/temperature history (i.e. the length of time $t$ the sample is annealed at a given temperature $T_a$ following a change in pressure $P$); it can be represented by the expression

$$T_{c, meas}(\delta, P, T_a, t) = T_{c, intrin}(\delta, P) + \Delta T_{c, relax}(\delta, P, T_a, t).$$

(2)

The first term on the right side gives the ideal or “intrinsic” change in $T_c$ which occurs imme-
diately following a change in pressure at any temperature, whereas the second “relaxation” term takes into account the change in $T_c$ from pressure-, temperature- and time-dependent relaxation effects. The simplest way to determine $T_{c,\text{intrin}}(P)$, the dependence which can be compared most directly with theory, is to carry out the entire experiment at a temperature low enough to eliminate (freeze out) all relaxation processes, so that $\Delta T_{c,\text{relax}} = 0$. As seen in Fig. 3, for Hg-1201 relaxation processes appear to be frozen out for $T \leq 200$ K. The two distinct “intrinsic” and “relaxation” contributions to $T_{c,\text{meas}}(P, T_a, t)$ for underdoped Hg-1201 can be easily recognized in Fig. 5 where the application of 0.79 GPa pressure at RT is seen to cause a larger change in $T_c$ than the pressure release below 90 K, corresponding to the pressure derivatives $(dT_c/dP)_{RT} \simeq (+1.41 \pm 0.14)$ K/GPa and $(dT_c/dP)_{LT} = (dT_{c,\text{intrin}}/dP) \simeq (+1.15 \pm 0.05)$ K/GPa, respectively.

Whereas in the underdoped sample the change in $T_c$ with pressure is linear, in Figs. 2a and 2b it is seen that for overdoped Hg-1201 there is a distinct change in the slope of $T_c(P)$ near 0.4 GPa for sample A and near 0.5 GPa for sample B. This evident nonlinearity is retained in the “intrinsic” $T_{c,\text{intrin}}(P)$ dependence obtained by releasing the pressure at low temperatures. This gives evidence that this nonlinearity is an intrinsic effect and does not have its origin in relaxation effects which occur at temperatures above 55 K, but may be due to a structural change. As pointed out previously, Cao et al. [10] also observe a nonlinearity in $T_c(P)$ near 0.5 GPa in strongly overdoped Hg-1201, but the change in slope is opposite in sign to the present results. Chen et al. [39] report a negative slope change in $T_c(P)$ near 0.5 GPa in nearly optimally doped Hg-1212. Recent neutron powder diffraction experiments under high pressure on Hg-1201 at variable oxygen content find no evidence for a structural phase transition to 1 GPa [40]; this study, however, did not include heavily overdoped samples with $T_c < 80$ K, as in both the present experiments and those of Cao et al. [10]. Further high-pressure structural studies are required to clarify the origin of the nonlinearity in $T_c(P)$.

The nonlinear $T_c(P)$ dependence and the notable change in $dT_c/dP$ in the present experiments on the two heavily overdoped Hg-1201 samples are but two of a number of indi-
cations that sufficiently overdoped Hg-1201 (where $T_c \leq 80$ K) possesses basic (structural) differences to underdoped Hg-1201. Cao et al. [10] have shown that the initial pressure derivative $dT_c/dP$ changes radically in the overdoped regime for $T_c \leq 80$ K. Xiong et al. [3] note that the $c$ lattice constant increases monotonically with oxygen content over the entire underdoped and partially overdoped regime, until $T_c \approx 80$ K is reached, remaining constant thereafter; the valence-bond sum technique for estimating carrier concentration also gives anomalous results for an oxygen content above this critical value. Xiong et al. [3] suggest that there may be two different types of lattice sites available for oxygen defects. In fact, recent powder neutron diffraction experiments on Hg-1201 by Jorgensen et al. [24] over a wide range of oxygen defect concentrations suggest that there are two competing oxygen defects in the Hg layer, an O3 defect in the center of the unit cell and an O4 defect nearer the cell’s edge. The relative concentrations of these defects switches with increasing $\delta$ upon passing from the underdoped region and through the maximum $T_c$, where O4 is the dominant defect, to the overdoped region where, at $T_c \approx 80$ K, O3 suddenly becomes the dominant defect. This “change of the defect” is mirrored in the dependence of $T_c$ on $\delta$ which deviates from the canonical inverted parabolic behavior. Of particular relevance to the present experiments is the fact that a sudden increase in the unit cell volume by $\sim 1\%$ accompanies this “change of the defect” $O4 \rightarrow O3$ at $T_c \approx 80$ K [24]. Since O3 should be the sole defect in our strongly overdoped samples, this implies that if sufficiently high pressure is applied, the O4 defect should become energetically favored over O3. In this picture the nonlinearity in $T_c(P)$ would signal a sudden changeover from a dominant O3 defect to O4. The fact that the critical onset pressure for sample B is somewhat larger (0.5 GPa) than for sample A (0.4 GPa) supports this picture since sample B is more strongly overdoped and thus the O3 defect more stable. Neutron diffraction experiments under high pressure conditions would be desirable to clarify the anomalous but interesting overdoped state in Hg-1201.

It is interesting to note that for under- and overdoped Hg-1201 with $T_c \approx 49$ K the initial “intrinsic” slopes $dT_c^{intrinsic}/dP = (dT_c/dP)_LT \approx -1.15 \pm 0.05$ K/GPa and $-1.15 \pm$
0.52 K/GPa, respectively, are equal in magnitude but opposite in sign. At first glance this result would appear to support a simple charge-transfer model \([5]\) in which \(dT_{c}^{\text{intrin}}/dP = (dT_{c}/dn)(dn/dP)\) and \(dn/dP = \text{constant} > 0\). However, this would lead to the expectation that \(dT_{c}^{\text{intrin}}/dP \simeq 0\) for an optimally doped sample (where \(dT_{c}/dn = 0\)), contrary to the experimental result that \(dT_{c}^{\text{intrin}}/dP \simeq +1.75 \pm 0.1\) K/GPa \([2]\). We note that the intrinsic pressure dependence for the more strongly overdoped sample B is only half the magnitude of that for sample A; the charge transfer model would lead to the expectation that \(dT_{c}^{\text{intrin}}/dP\) should be greater in magnitude, contrary to experiment. It is certainly possible that pressure-dependent shifts in the defect structure in Hg-1201 play a role here. Further measurements of \(T_{c}(P)\) together with systematic structural studies under high pressure are needed to resolve this issue.

**B. Relaxation Behavior at Ambient Pressure**

In order to better characterize the relaxation behavior at different pressures and temperatures in overdoped Hg-1201, we calculate the pressure-dependent activation energy \(E_{A}(P)\) from the measured values of the relaxation time \(\tau(T, P)\) at a given temperature using the Arrhenius law

\[
\tau(T, P) = \tau_{0} \cdot \exp \left\{ \frac{E_{A}(P)}{k_{B}T} \right\} .
\]

We set the attempt period \(\tau_{0}\) equal to the value \((\tau_{0} \approx 1.4 \times 10^{-12} \text{ s})\) found in earlier temperature-quench experiments on Y-123 \([14]\). Using the values of the relaxation times at ambient pressure from the previous section, the corresponding activation energy for overdoped (sample A) and underdoped Hg-1201 can be calculated using Eq. 3, yielding \(E_{A}(1 \text{ bar}) \simeq 0.84 \text{ eV}\) and \(0.90 \text{ eV}\), respectively. These values are quite comparable to each other and to activation energies determined from relaxation studies on Y-123 \((0.97 \text{ eV})\) \([14,16]\), Tl-2201 \((0.72 \text{ eV})\) \([23]\) and Tl-1212 \((0.86 \text{ eV})\) \([17]\), as well as to oxygen tracer diffusion studies on Y-123 and other oxide superconductors \([11]\). This fact, and the known sensitivity
of the relaxation behavior to the oxygen content \cite{13,16}, make it likely that the above relaxation effects originate in the oxygen sublattice. To our knowledge, no attempt has yet been made to compute the energy barrier for oxygen diffusion in Hg-1201; in a recent model calculation Islam and Winch \cite{12} have estimated $E_A(1\text{ bar}) \approx 0.68\text{ eV}$ for the migration of interstitial O(4) oxygen in the three-layer compound Hg-1223, a value roughly comparable to our present result for Hg-1201.

It is interesting to note that no relaxation whatsoever has been observed in $T_c$ for optimally doped Hg-1201 \cite{2} or, for that matter, for any other optimally doped oxide superconductor studied to date \cite{8,13,16,17}. Does this mean that in optimally doped samples relaxation phenomena do not occur? Certainly not! The absence of relaxation phenomena in $T_c$ for optimally doped samples can be readily understood if the change in $T_c$ due to relaxation phenomena originates primarily from a change in the carrier concentration $n$ in the CuO$_2$ plane(s); Hall effect studies on Tl-2201 support this conclusion \cite{13}. In an optimally doped sample the value of $T_c$ is maximized as a function of $n$, i.e. $T_c(n)$ is at an extremum where $(dT_c/dn) = 0$, so that $(dT_c/dP)^{relax} \approx (dT_c/dn)(dn/dP)^{relax} \approx 0$. In optimally doped samples, therefore, relaxation processes in the oxygen sublattice initially cause no change in $T_c$, but should have a measurable effect on other properties such as the electrical resistivity, Hall coefficient, lattice parameters, etc. In this regard further studies on the Hg-oxides would be of particular interest since optimal doping occurs at a finite concentration of oxygen defects, in contrast to Y-123 and Tl-1201 which are nearly devoid of oxygen defects when $T_c$ is at its maximum value.

An important question remaining is to identify the mechanism by which the relaxation processes change the carrier concentration in Hg-1201. For Y-123 Veal and Paulikas \cite{14} proposed that the local rearrangement of oxygen anions in the CuO chain layer causes the valence of the ambivalent Cu$^{1+/2+}$ cations in this layer to change. The maintenance of overall charge neutrality then dictates that the charge carrier concentration in the CuO$_2$ layers must adjust accordingly. In Tl-2201 the oxygen defects are incorporated interstitially in the Tl$_2$O$_2$ double-layer \cite{15}; some form of local ordering of these oxygen would then
prompt some of the ambivalent Tl$^{3+}$-cations in this layer to decrease their valence by drawing electron charge away from the CuO$_2$ plane (for thallium +1 and +3 are the preferred valence states). The presence of ambivalent cations would not appear to be mandatory for charge transfer to occur, but probably serves to enhance it; as pointed out in the Introduction, relaxation phenomena have been reported in superoxygenated La$_2$CuO$_{4+y}$ [21], although this compound contains no ambivalent cations outside the CuO$_2$ layer. Hg-1201 would appear to be a further such example, since XPS studies [46] on an optimally doped sample indicate that the valence of Hg is 2+. Further evidence against Hg cation ambivalence in Hg-oxides is given by chemical analysis on a series of Hg-1212 samples near optimal doping which show that the average Cu valence increases with oxygen content, but that the valence of Hg is fixed at 2+ [17]. Two possible mechanisms for the observed weak relaxation phenomena in Hg-1201 are: (1) the degree of oxygen ordering may directly influence how the available hole carriers are distributed between the CuO$_2$ planes and other structural elements [20]; (2) ambivalent Cu$^{1+/2+}$ cations on Hg sites may switch their valence as oxygen defects rearrange. Indeed, studies by Wagner et al. [26] show that there is a substitutional defect in Hg-1201 in the form of a partial substitution of Cu ions on the Hg site; the same overdoped Hg-1201 sample A used in the present experiments was found to contain a substitution of $\sim 8\%$ of Cu on the Hg site [27] which could conceivably lead to modest relaxation effects of the order $\sim 8\%$ of that expected for full substitution. It is interesting to note that in the present experiment on overdoped Hg-1201 (sample A) the magnitude of the observed relaxation derivative \((dT_c/dP)_{\text{relax}} \approx -0.3 \text{ K/GPa}\) is only $\sim 10\%$ of that for Y-123 [16] with a similar value of $T_c$. A critical test would be to study non optimally doped Hg-1201 samples devoid of Cu substitution; if the second scenario is correct, there would then be no relaxation in $T_c$. 
C. Relaxation Behavior under High Pressure

Using the values of $\tau(T, P)$ for overdoped Hg-1201 (sample A) from the previous section, $E_A(P)$ is calculated using Eq. 3 and displayed in Fig. 6. We ignore any change in $\tau_o$ with pressure since its anticipated decrease under pressure is very small [18]. In this figure the value of the pressure near the annealing temperature $T_a$, rather than the value near $T_c$, is used since below 250 K only insignificant relaxation occurs. Assuming that, as found previously for Y-123 [31], $E_A$ is a linear function of pressure, we obtain $dE_A/dP \simeq (+114 \pm 50)$ meV/GPa (dashed line in Fig. 6). To our knowledge, the only other such study on a superconducting oxide was on strongly underdoped YBa$_2$Cu$_3$O$_{6.41}$ [31] where we found $dE_A/dP \simeq (+44 \pm 2)$ meV/GPa, approximately half the present value for Hg-1201.

The pressure dependence of relaxation behavior is normally analyzed in terms of an activation volume $\Delta V_A$ which can be calculated from the pressure dependence of the activation energy [19]

$$\Delta V_A = \Delta V_f + \Delta V_m = N_A \left( \frac{\partial E_A}{\partial P} \right),$$

where $\Delta V_f$ is the change in volume due to the formation of a vacancy or interstitial, $\Delta V_m$ is the volume change due to the migration of the diffusing atom, and $N_A$ is Avogadro’s number. If we assume that the oxygen defects involved in the relaxation phenomena are already present and need not be created, then $\Delta V_f = 0$. As discussed above, two distinct types of oxygen defect have been found in the HgO layer in Hg-1201 [27,24], with a transition from one type to the other near the optimal doping concentration. The nonlinearity in $T_c(P)$ seen in Fig. 2 near 0.4 GPa for the overdoped samples may signal a transition from the O3 to O4 defect type. Since in the present experiments the time dependence of the relaxation behavior was only studied for pressures below 0.3 GPa, we assume that only a single oxygen defect type is responsible for the relaxation, so that $\Delta V_f = 0$. From Eq. (4) we now estimate from the above value of $dE_A/dP$ the molar activation volume to be $\Delta V_A \approx \Delta V_m \simeq + (11.0 \pm 4.8)$ cm$^3$/mol which is approximately twice the molar volume of the diffusing O$^{2-}$.
ion (5.78 cm$^3$/mol [50]). In our recent study on underdoped YBa$_2$Cu$_3$O$_{6.41}$ an activation volume of + 4.2 cm$^3$/mol [31] was obtained.

A positive migration volume $\Delta V_m$ implies that the lattice increases in volume as a diffusing ion passes over a saddle point in moving from one site to another. It is physically reasonable that diffusion slows under pressure ($dE_A/dP > 0$) because squeezing the lattice together leaves less space through which the interstitial atoms can diffuse. Indeed, in ionic compounds [51], such as the oxide superconductors, a positive activation volume is normally observed. However, an enhancement of the diffusion rate under pressure (negative activation volume) may be observed in covalently bonded substances, such as amorphous Si [52]. Recently, the activation volume for both Hg-1201 and Y-123 has been calculated [38] using a hard sphere model to estimate the local expansion in the lattice as the oxygen defect travels along its diffusion path. For both systems the measured values of $\Delta V_A$ are underestimated by a factor of two to three in this model.

In summary, the present experiments on Hg-1201 give evidence for weak relaxation phenomena in the transition temperature for both under- and overdoped samples; these relaxation effects are opposite in sign but roughly equal in magnitude and involve similar activation energies. This result, plus the absence of relaxation effects in $T_c$ for optimally doped Hg-1201 [2], support the view that relaxation phenomena influence $T_c$ via the transfer of charge in or out of the CuO$_2$ planes. The relaxation time at ambient pressure is found to be approximately 4 h at 265 K and increases strongly with pressure. This pressure dependence can be expressed in terms of an activation volume equal to + 11.0 cm$^3$/mol. An anomalous nonlinearity in $T_c(P)$ is observed for the overdoped samples near 0.4 GPa which may indicate a transition from one oxygen defect type to another.

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**FIGURE CAPTIONS**

**Fig. 1.** Real part of the ac-susceptibility versus temperature for overdoped Hg-1201 (sample A) at ambient pressure. Data points become very dense above 40 K. Solid line is guide to the eye. The inset shows a blow-up of the data near the superconducting onset temperature $T_c$.

**Fig. 2.** Dependence of $T_c$ on hydrostatic pressure for two samples of overdoped Hg-1201: (a) $T_c$(1 bar) $\simeq$ 47.8 K (sample A); pressure was successively increased at 298 K (o) and then successively decreased at either 298 K (■) or at temperatures <55 K (●). (b) $T_c$(1 bar) $\simeq$ 40.0 K (sample B); pressure was successively increased at 298 K (o) and then successively decreased at temperatures <65 K (●), with numbers giving the order of measurement. Pressure was then reapplied (△) at 298 K and released (▲) at T <65 K, as before. See text for full details. Solid lines are guides to the eye.

**Fig. 3.** Dependence of $T_c$ on annealing temperature $T_a$ in overdoped Hg-1201 (sample A) following the application of pressure at 298 K and its removal at 50 K. Relaxation effects are only observed for temperatures above 200 K. Numbers give order of measurement. Dashed and solid lines are guides to the eye.

**Fig. 4.** Relaxation data on overdoped Hg-1201 (sample A) at three different pressures. The solid lines give fits using Eq. (1) with given values of $\tau$. Numbers give order of measurement. See text for details.

**Fig. 5.** Dependence of $T_c$ on pressure in underdoped Hg-1201 where 0.7 GPa pressure is applied at 298 K but released at temperatures below 90 K. Numbers give order of measurement. Dashed and solid lines are guides to the eye. See text for details.

**Fig. 6.** Activation energy versus pressure for overdoped Hg-1201 (sample A). Dashed line gives best linear fit to data.
$\chi'(10^{-3}\text{ emu/g})$

$T_c = 47.81\text{ K}$

Hg-1201 overdoped
Hg-1201 overdoped sample B

T_c (K)

P (GPa)

< 65 K

298 K

anneal at RT

1

2

3

4

5

6

7

8

9

10

11

12

13
Hg-1201 overdoped

apply 0.67 GPa at 298 K

release P at 50 K
(a) $T_c = 47.7 K$, $\tau = 3.4 h$, $T_a = 265 K$, $0 GPa$

(b) $T_c = 47.5 K$, $\tau = 17.5 h$, $0.15 GPa$, $T_a = 265 K$

(c) $T_c = 47.5 K$, $\tau = 0.9 h$, $0.30 GPa$, $T_a = 285 K$
Hg-1201 overdoped