

PRESSURE-INDUCED OXYGEN ORDERING EFFECTS IN HIGH- T_c SUPERCONDUCTORS

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Oxygen defects in the superconducting oxides are known to exhibit considerable mobility at room temperature. In some systems this high mobility leads to local oxygen ordering effects when hydrostatic pressure is applied at ambient temperature and results in anomalously large changes in T_c . Recent experiments on $\text{Th}_2\text{Ba}_2\text{CuO}_{6+\delta}$ reveal the existence of two distinct oxygen ordering processes which become activated for temperatures above 60 K and 150 K, respectively. Evidence is discussed for the existence of oxygen ordering processes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which may be responsible for the phenomena of both transient and persistent photo-induced superconductivity.

One of the more promising strategies for furthering our understanding of the superconducting state in the high- T_c oxides is to search for systematics in the variation of the transition temperature T_c with parameters such as the concentration n of charge carriers per CuO_2 -plane or the applied pressure P .^{1,2} Unfortunately, the true dependence of T_c on n or P valid for an ideal isostructural system is sometimes masked by atomic rearrangements or structural phase transitions, some of which occur in the oxygen sublattice.¹ In spite of these difficulties, systematic experimentation has revealed that the true dependence of T_c on n or P is remarkably simple. For hole-doped oxide superconductors, T_c appears to be a parabolic function of n ,³

$$T_c \simeq T_c^{\max} [1 - 82.6(n - 0.16)^2], \quad (1)$$

as seen in Figure 1. The hole-carrier content n in the oxides can be enhanced in one of three ways: cation substitution, as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,⁴ an increase in oxygen content,⁵ or the application of high pressure.⁶

Murayama et al.⁶ find in high-pressure Hall-effect studies on oxide superconductors that typically $d \ln n / dP \approx +10 \text{ \% / GPa}$. This observed increase in n under pressure would lead to the expectation from Eq.1 that $dT_c/dP > 0$ for underdoped ($n < n_{\text{opt}}$), $dT_c/dP = 0$ for optimally doped ($n = n_{\text{opt}}$), and $dT_c/dP < 0$ for overdoped ($n > n_{\text{opt}}$) samples. Unfortunately, as indicated in Fig.1, this simple charge-transfer model does not agree well with experiment. For optimally doped ideal samples, where no pressure-induced phase transitions are known to occur, it is typically found that $dT_c/dP \approx +1$ to $+3 \text{ K/GPa}$,^{1,7,8,9,10} implying that T_c must depend on further variables

than n . As indicated in Fig.1, underdoped samples tend to have more positive values of dT_c/dP and

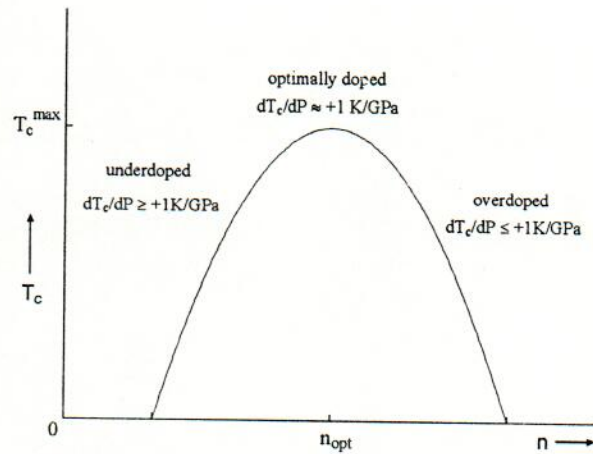


Figure 1: Dependence of T_c on hole-carrier content n according to Eq.1. Representative experimental values of dT_c/dP for underdoped, optimally doped and overdoped oxides are given. $T_c = T_c^{\max}$ when $n = n_{\text{opt}}$

overdoped samples more negative values. These observations for cation substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y-123) prompted Neumeier and Zimmermann⁷ to propose that there are two primary contributions to the pressure derivative of dT_c/dP , one reflecting the increase of n with pressure and another "intrinsic" contribution arising from all other sources, namely

$$\frac{dT_c}{dP} = \left(\frac{dT_c}{dn} \right) \left(\frac{dn}{dP} \right) + \left(\frac{dT_c}{dP} \right)^{\text{int}}. \quad (2)$$

Since $dT_c/dn = 0$ for an optimally doped sample, Eq.2 implies that $(dT_c/dP)^{\text{int}} = dT_c/dP \simeq +1$ to $+3 \text{ K/GPa}$. Using known or estimated val-

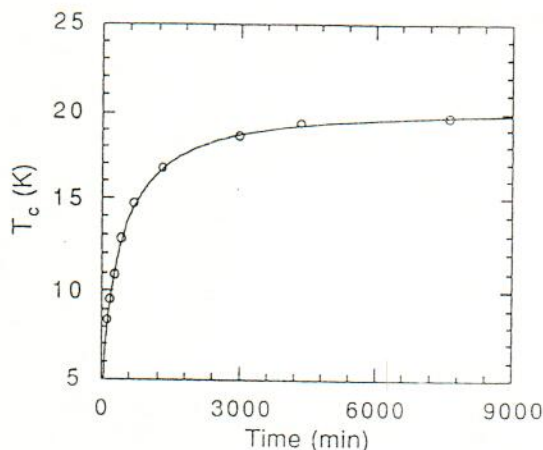


Figure 2: T_c as function of annealing time t at room temperature for a quenched sample of $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ (Ref.15).

the bulk modulus B ,¹¹ Klehe et al.^{12,13} have obtained the following values of the exponent α in $T_c \propto V^{-\alpha}$ for the intrinsic dependence of T_c on sample volume V at constant n : $\text{HgBa}_2\text{CuO}_{4+\delta}$ (-1.22 ± 0.05), $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (-1.19 ± 0.06), $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (-1.20 ± 0.05), $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (-1.25 ± 0.06), $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (-1.35 ± 0.4), $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ (-0.9 ± 0.2), $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (-1.16 ± 0.3), $(\text{Bi}_{1.8}\text{Pb}_{0.4})\text{Sr}_{1.85}\text{Ca}_{2.05}\text{Cu}_3\text{O}_{10+\delta}$ (-1.36), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (-1.04 ± 0.15). This simple approximate result that $T_c \propto V^{-1.2}$ must be accounted for by any theory claiming to describe the superconducting state in the oxides.

As stated above, the true dependence of T_c on a given parameter can be masked by concomitant structural changes. In this paper we would like to summarize the existing evidence that in some, and perhaps many, high- T_c oxides the application of pressure causes a redistribution within the oxygen sublattice which can lead to changes in both n and T_c .

In the high- T_c superconductors it is well known that oxygen defects possess a sizeable mobility, even at room temperature (RT).¹⁴ As seen in Fig.2, oxygen vacancy ordering in underdoped Y-123 leads to an increase in T_c by $\sim 20\text{K}$ if the sample is annealed at RT for sufficient time following a quench to 77K from high temperature.¹⁵ This enhancement in T_c is believed to arise from local oxygen ordering in the CuO -chains which leads to an increase in the number of Cu^{1+} relative to

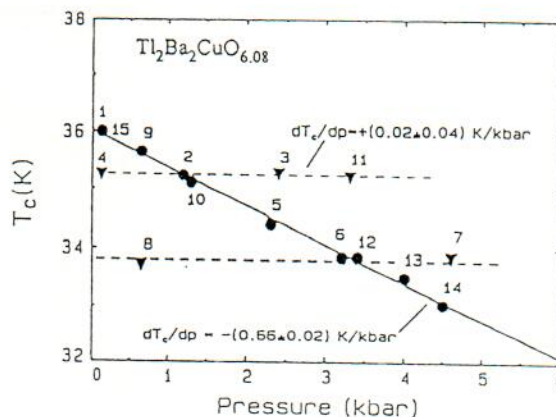


Figure 3: T_c versus pressure for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6.08}$ from Ref.17. Regarding oxygen content, see caption for Fig.4. Numbers give order of measurement. Points give data for pressure change at room temperature. Triangles give data for pressure change at low temperature (50K).

Cu^{2+} in these chains, thereby increasing the hole-carrier density n in the superconducting CuO_2 -planes.¹⁶ From the data in Fig.2, an activation energy $E_A \approx 1\text{eV}$ can be estimated,^{15,16} in excellent agreement with tracer diffusion experiments.¹⁴

Following these studies on the influence of thermal history on oxygen defect ordering, Sieburger and Schilling¹⁷ found that the application of hydrostatic pressure can also influence the degree of oxygen defect ordering. They studied the pressure dependence of T_c for polycrystalline $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Tl-2201) using a He-gas pressure system (Unipress, Warsaw) which allows precise pressure changes over a wide temperature range. As seen in Fig.3, if the pressure is applied or released at RT, T_c changes reversibly with pressure at the rate $(dT_c/dP)_{RT} \simeq -6.6\text{ K/GPa}$. If, however, the pressure is varied at low temperatures (LT) near 50K, no change in T_c occurs. The pressure derivative dT_c/dP thus depends in both magnitude and sign on the temperature at which the pressure is changed! Further studies on Tl-2201 revealed that $(dT_c/dP)_{RT}$ is a strong function of the oxygen content, as seen in Fig.4. For $\delta = 0$ or 0.11, the two pressure derivatives $(dT_c/dP)_{RT}$ and $(dT_c/dP)_{LT}$ are seen to assume the same values.

That these anomalous results are not due to the polycrystallinity of the samples is shown by very recent studies¹⁸ on a Tl-2201 single crystal (Figs.5 and 6) where the sharp superconducting transition in the ac-susceptibility is seen to shift

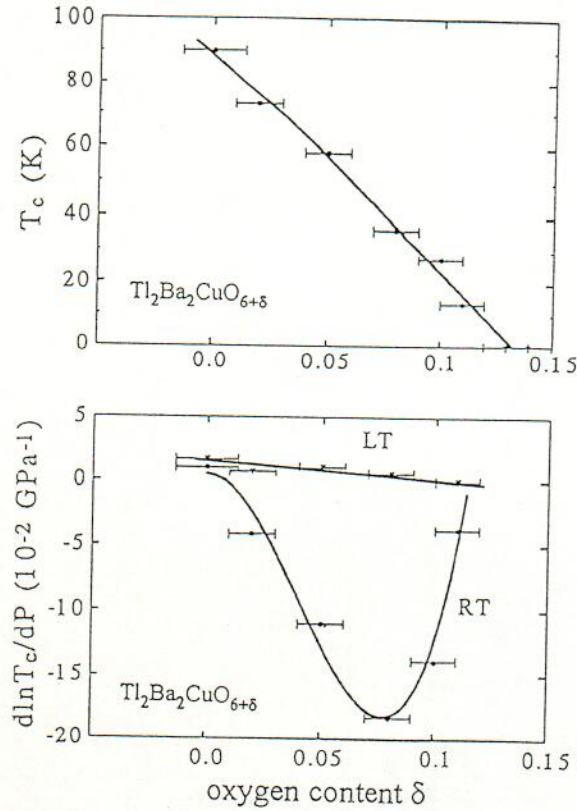


Figure 4: Dependence of T_c (upper) and the relative pressure dependence $d\ln T_c/dP$ (lower) on oxygen content δ in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ for pressure change at both low (LT) and ambient (RT) temperature.

plied at RT, but to *decrease* slightly further if the pressure is released at LT (55K). Our interpretation of these results has been¹⁷ that the application of pressure at RT results in the usual moderate changes in T_c for an ideal isostructural sample, as described above, *plus* an anomalous decrease in T_c due to pressure-induced oxygen ordering. This ordering results in a significant additional increase in n which leads to an enhanced decrease in T_c for overdoped samples (see Fig.4). On the other hand, if the pressure is changed at LT ($\sim 50\text{K}$), the oxygen is frozen in place and thus is unable to order when pressure is applied. This scenario has received strong support from neutron diffraction studies on Tl-2201 in a He-gas system where the lattice parameters are found to depend markedly on the T-P history.¹⁹

Returning to Fig.6, following the release of

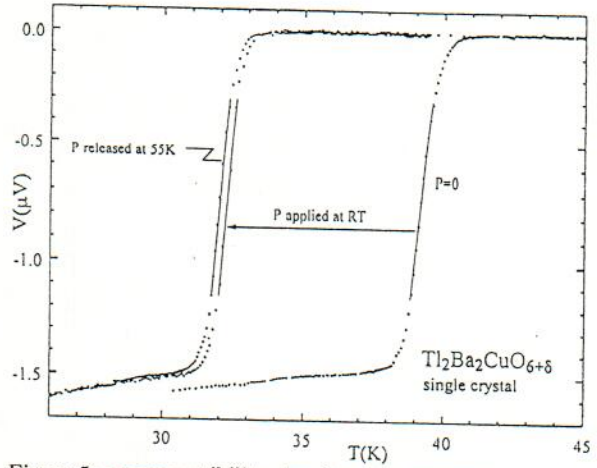


Figure 5: ac susceptibility signal versus temperature for a Tl-2201 single crystal showing the transition to superconductivity at different pressures. $H_{ac} = 0.15 \text{ Oe}$.

pressure at LT (55K), the Tl-2201 crystal was annealed at progressively higher temperatures T_{anneal} , normally for 1 hour (h), before cooling down to determine T_c . This relaxation is seen in more detail in Fig.7. At selected temperatures additional annealing was carried out for the total times given in the figure. The essential (and unexpected) result here is that the relaxation takes place in two separate temperature regimes, a LT regime $60\text{K} \leq T_{\text{anneal}} \leq 105\text{K}$ and a HT regime $170\text{K} \leq T_{\text{anneal}} \leq 270\text{K}$, with a plateau inbetween. This clearly points to the existence of two distinct relaxation processes within the oxygen sublattice. This two-step relaxation phenomenon was first observed by Klehe et al.^{13,18,20} on a polycrystalline Tl-2201 sample with $T_c(0) \simeq 23\text{K}$. From these studies we estimate that for the LT relaxation processes, the activation energy is $E_A \simeq 0.25\text{eV}$, whereas for the HT processes, $E_A \simeq 0.72\text{eV}$. A complete exposition of these results is given in a separate publication.¹⁸

The crystal structure of Tl-2201 is shown in Fig.8. The superconducting CuO_2 layer is situated between two Tl_2O_2 double layers which act as charge reservoirs. Varying the oxygen content in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ changes the amount δ of interstitial oxygen within the Tl_2O_2 double layer. Since the anomalous effects in dT_c/dP appear to disappear for $\delta \simeq 0$ or 0.11 , as seen in Fig.4, it would seem likely that it is the interstitial oxygen O(4) which is ordering rather than the oxygen O(3) in the Tl_2O_2 planes. The concentration $\delta \simeq 0.11$ cor-

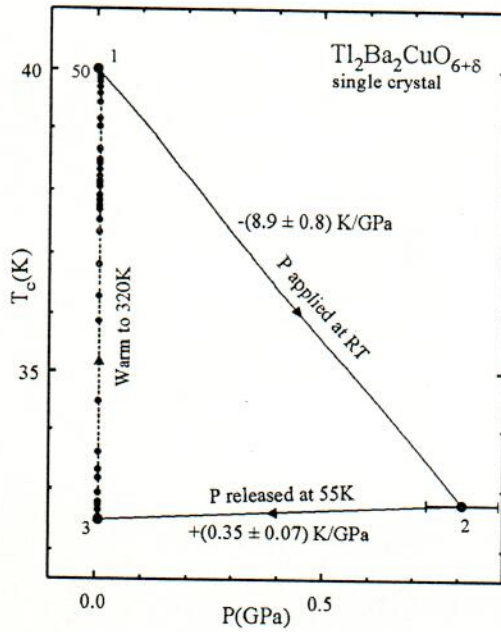


Figure 6: Dependence of T_c on pressure for a Tl-2201 crystal. Data points and arrows give order of measurement.

responds to one interstitial oxygen per nine unit cells in a plane. This may be a particularly stable configuration which inhibits pressure-induced interstitial oxygen ordering. However, in Fig. 4 it is seen that for $\delta = 0$ the sample is optimally doped and T_c takes on its maximum value (~ 92 K). From Fig. 1 we see that in this case an increase in n , even if anomalously large, would to first order cause no change in T_c , so that any effects of oxygen ordering on n would be expected to have little or no influence on T_c . In fact, parallel Hall-effect studies^{13,18,21} have shown that it is the change in n through oxygen ordering which primarily affects T_c . In addition, as we discuss below, for samples with high transition temperatures, $T_c \gtrsim 90$ K, a sizeable, if not dominant, portion of the oxygen ordering may no longer be frozen in at temperatures comparable with T_c . It is thus not yet clear whether the interstitial O(4) or the planar O(3) oxygen are primarily responsible for the ordering effects observed. A discussion of the mechanism by which oxygen ordering affects n in Tl-2201 as well as a model for short-range oxygen ordering effects involving the planar O(3) oxygen in the Ti_2O_2 double layer has been given by A.-K. Klehe at this conference.²²

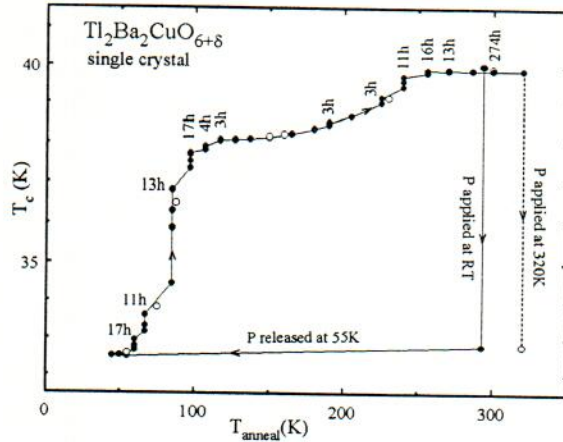


Figure 7: Data from Fig. 6 replotted as T_c versus annealing temperature. Two data series are shown, (○) following (●).

Since the HT relaxation mode in Tl-2201 involves activation energies $E_A \simeq 0.72$ eV near those obtained in tracer diffusion experiments ($E_A \simeq 1$ eV) on other high- T_c oxides, it would seem likely that the HT processes involve the migration of O(3) or O(4) oxygen from one unit cell to another. On the other hand, the very low value $E_A \simeq 0.25$ eV for the LT relaxation modes would speak for ordering processes whereby the oxygen ions never leave the unit cell but rather shift from one equivalent site to another *within* the unit cell (see Fig. 8).^{13,22}

The phenomena of pressure-induced oxygen ordering is not restricted to the single system Tl-2201, but has also been found to occur in superoxygenated $\text{La}_2\text{CuO}_{4+\delta}$,²³ in oxygen depleted Y-123,²⁴ and most recently in $\text{Ti}_2\text{Sr}_2(\text{Ti}_{0.8}\text{Ca}_{0.2})\text{Cu}_2\text{O}_{6.86}$.¹⁸ Other than for Tl-2201, it has not yet been determined in which temperature regime the oxygen ordering processes are activated when pressure is applied.

We would like to emphasize that oxygen ordering phenomena, whether activated by annealing temperature-quenched samples or by applying high pressure, may occur to some extent in many, if not all, superconducting oxides. This does not, however, necessarily imply that this oxygen redistribution will lead to a measurable change in n or T_c . For n or T_c to change it is necessary both that an ambivalent cation, like thallium (Ti^{1+} or Ti^{3+}) or copper (Cu^{1+} or Cu^{3+} in the chains of Y-123), be present in the charge reser-

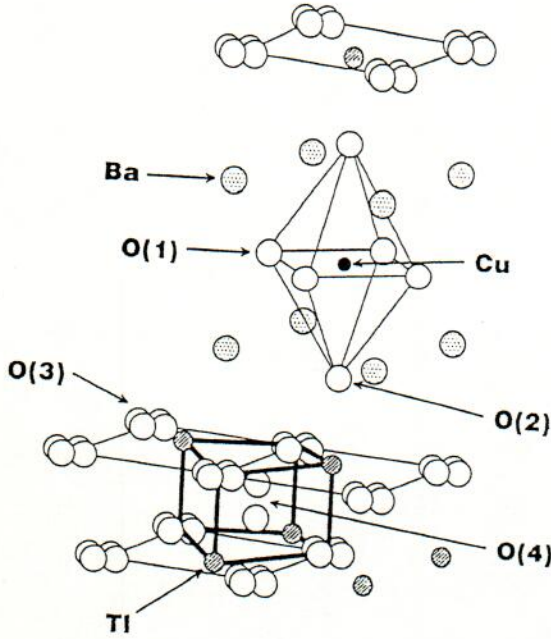


Figure 8: Crystal structure of Tl-2201 from Ref.25. Each oxygen O(3) in the Tl_2O_2 -double layer has four equivalent positions. Each interstitial oxygen O(4) within the double layer has two equivalent positions.

voir and that the local oxygen ordering be capable of switching the nearby cation from one valence state to another.²² This may be the reason why $(dT_c/dP)_{LT} \simeq (dT_c/dP)_{RT}$ in Bi-2212: local oxygen ordering is not capable, for energetic reasons, of switching bismuth between Bi^{3+} and Bi^{5+} .⁹ What does the cation valence have to do with the hole-carrier density n in the CuO_2 -planes? As the O(3) or O(4) oxygen in Tl-2201 order when pressure is applied at RT, some Tl-ions will switch from a Tl^{3+} to a Tl^{1+} valence state, thus tying up two additional electrons which must come from the CuO_2 -plane, i.e. an increase in the density of holes.^{13,22}

Another reason that oxygen ordering effects have been observed in relatively few high- T_c oxides may be that for many systems the values of T_c are simply so high that most of the ordering has been annealed out at temperatures below T_c . Indeed, in Tl-2212 ($T_c^{\text{max}} \simeq 115\text{K}$) and Tl-2223 ($T_c^{\text{max}} \simeq 125\text{K}$) the values of T_c lie well above the entire temperature region $60\text{K} \leq T_{\text{anneal}} \leq 105\text{K}$ where the LT relaxation in Tl-2201 is observed. In the Hg-based superconductors the stability of the

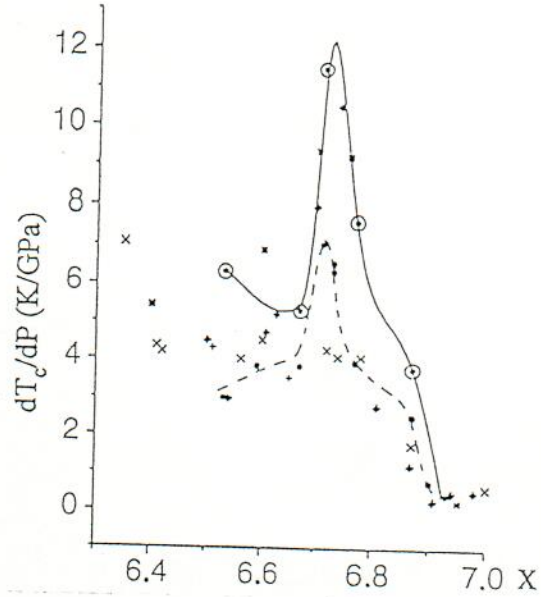


Figure 9: Pressure derivative of T_c for $\text{YBa}_2\text{Cu}_3\text{O}_x$ as function of oxygen content x from Ref.24. Solid line through data when pressure applied at RT, dashed line when pressure applied at 90K.

Hg^{2+} valence state may account for the apparent lack of pressure-induced oxygen ordering effects.²²

Recent internal friction measurements on Tl-2201 give some evidence for a LT relaxation peak, but further studies are needed.²⁶ LT relaxation peaks have been observed at $E_A \approx 0.28\text{eV}$ for Bi-2212 and at $E_A \approx 0.08, 0.12$, and 0.18eV for Y-123.²⁷ In addition, we find what we believe to be evidence for both HT and LT relaxation effects in the extensive high-pressure data on underoxygenated Y-123 recently published by Fietz et al.,²⁴ and shown in Fig.9. In their detailed study of $T_c(P)$ over a wide range of oxygen concentrations, the value of $(dT_c/dP)_{RT}$ is found to be strongly peaked at the very large value $+12\text{ K/GPa}$ for the oxygen content $\text{O}_{6.7}$. It is interesting to note that the pressure derivative $(dT_c/dP)_{90\text{K}}$, where the pressure is changed at 90K instead of RT, is diminished for all oxygen concentrations, but is still peaked at $\text{O}_{6.7}$. We believe that the existence of this residual peak provides clear evidence that pressure-induced oxygen relaxation phenomena occur in Y-123 at temperatures below 90 K, in analogy with our findings for Tl-2201. In fact, we would like to suggest that the existence of both

LT and HT relaxation modes in Y-123 may provide the key to understanding the phenomena of both transient and persistent photo-induced superconductivity in this compound.²⁸ In particular, relaxation processes with activation energies at or below 0.1 eV could result in nanosecond relaxation times at 90 K.

The above results on Tl- and Y-based systems indicate that, on both fundamental and applied levels, oxygen ordering effects may play an important role in the superconductivity of many high- T_c oxides. Further experiments are currently being carried out to enhance our understanding of these interesting phenomena.

This research is supported by the National Science Foundation under grant DMR 95-09885.

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