# Dependence of $T_c$ on hydrostatic pressure in a 123 superconductor

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**Abstract.** Hydrostatic pressure studies on the tetragonal 123 superconductor  $(La_{1-x}Ca_x)$   $(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$  for x = 0.1 and variable oxygen content y show that  $T_c$  increases rapidly under pressure (+5 K/GPa) for underdoped, optimally doped and overdoped samples. This points to a common cause for the pressure-induced changes in the superconductivity at all levels of doping, with negligible effects from charge transfer. Weak relaxation behavior in  $T_c$  is observed only for the most underdoped sample.

PACS. 74.62.-c Transition temperature variations – 74.62.Fj Pressure effects – 74.72.Jt Other cuprates

## 1 Introduction

Of particular value to enhance our understanding of high- $T_c$  superconductors (HTSC) are systematic studies of both normal and superconducting properties over the widest possible doping range. Unfortunately, only very few HTSC permit a sufficient degree of cation substitution or variation in the oxygen concentration to cover the entire underdoped to overdoped region where  $T_{\rm c}$  increases from zero Kelvin, passes through a maximum, and falls again to zero. One of these rare systems is the 123 compound  $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$  (CLBLCO) which, unlike  $YBa_2Cu_3O_{\mu}$  (YBCO), allows within a single phase cation substitutions over the range  $0 \le x \le 0.4$ with variable oxygen content up to  $y \simeq 7.3$  [1]. As seen in Figure 1, for x = 0.1 the value of  $T_c$  in this system traverses the entire underdoped to overdoped range as a function of the oxygen content. A further advantage of CLBLCO over YBCO is the absence of the CuO chains which lead to the latter's orthorhombicity and a complicated dependence of  $T_{\rm c}$  on oxygen content. CLBLCO takes on the tetragonal structure and, as seen in Figure 1, the dependence of  $T_{\rm c}$  on y displays the approximate inverted parabolic dependence found for many HTSC [3]. Because of the inherent simplicity of this system, extensive systematic studies of its properties in the normal and superconducting state should provide important information. An example for this is given by a very recent comparative study on CLBLCO which reveals that both  $T_{\rm c}$  and the degree of  $CuO_2$  plane buckling pass through a maximum at the same value of y, suggesting a common origin for both phenomena [4].



Fig. 1. Dependence of  $T_c$  from the onset to superconductivity in the electrical resistivity on oxygen content y in tetragonal  $(\text{La}_{1-x}\text{Ca}_x)(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$  for x = 0.1. High pressure experiments have been carried out on samples in present studies ( $\circ$ ) and in previous studies ( $\times$ ) in reference [9].

The pressure dependence of  $T_c$  reflects the change with lattice parameter of those solid state properties responsible for the superconducting state, including the pairing mechanism itself [5]. In HTSC several distinct properties relevant to superconductivity may change under pressure, including the number of carriers in the CuO<sub>2</sub>-plane(s), the density of carriers in these planes, the degree of plane buckling, etc. To further complicate matters, the number of carriers may not be a unique function of pressure but may depend on the temperature at which the pressure is changed, *i.e.*  $T_c(P)$  may depend on the entire

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pressure/temperature/time history of the experiment! These latter effects are believed to be caused by changes in the distribution of mobile oxygen defects as the pressure is varied [5,6]. Because of the existence of the ortho-I and ortho-II chain structures in underdoped YBCO which are formed by mobile oxygen defects in the basal plane, the dependence of  $T_c$  on both oxygen content y and applied pressure is extraordinarily complex [7]. Very recent highpressure studies to 17 GPa on YBCO show that  $T_c(P)$ changes markedly with both the oxygen content y and the temperature at which the pressure is applied [8]. It is very difficult to glean information of fundamental importance from the complex  $T_c(P)$ -dependence of YBCO.

The interpretation of  $T_{\rm c}(P)$ -data on CLBLCO should be relatively straightforward because of the simplicity of the tetragonal structure which it retains throughout its phase diagram. Earlier studies by Goldschmidt et al. [9] determined  $T_{\rm c}(P)$  on this system to 0.8 GPa for several different values of x but over a very limited range of oxygen content y. In the present study we focus our attention on three CLBLCO samples with x = 0.1 and varying oxygen content, two being nearly equally under- and overdoped with onsets in the ac susceptibility at  $T_{\rm c} \simeq 21.6$  K and 26.2 K, respectively, and the third being optimally doped with  $T_{\rm c} \simeq 52.3$  K. Surprisingly,  $T_{\rm c}$  is found to increase rapidly with pressure by approximately the same amount ( $\sim +5$  K/GPa) for all three samples with only the underdoped sample displaying weak pressure-induced relaxation phenomena. This result suggests that a single mechanism is responsible for the enhancement of  $T_{\rm c}$  under pressure with only minor effects from pressure-induced charge transfer. One possible mechanism would be a decrease in the degree of plane buckling as pressure is applied, a possibility which could be checked by neutron diffraction studies under high-pressure conditions.

# 2 Experiment

The CLBLCO samples with x = 0.1 were prepared by the usual carbonate-oxide method. The starting materials are  $La_2O_3$  which is 99.98% pure and free of hydroxide after preheating at 1000 °C to 1050 °C for a few days, CuO 99+% pure, BaCO<sub>3</sub> 99% pure (preheated at 900 °C for one day, during which the volume decreases), and  $CaCO_3$ 99+% pure (preheated at 450 °C until constant weight was achieved in order to remove traces of water). The preheated compounds were cooled in a desiccator. Stoichiometric proportions of these compounds were first ground using a zirconia planetary ballmill and then fired in air three times at 950 °C for 16 to 20 hours in a box furnace. After each firing they were transferred from the hot furnace to a desiccator and reground with an agate mortar and pestle. The fired powders were pelletized into bars of dimensions  $2.5 \times 2.5 \times 13 \text{ mm}^3$  (weight 0.4 g) under a pressure of 0.6 GPa. The pellets were sintered in dry oxygen at 960 °C for 60 hours and slowly cooled to room temperature at a rate of 10 °C/hour. The underdoped sample

was prepared by reducing the as-prepared pellet in oxygen at 450 °C for 27 hours and quenching it to liquid nitrogen temperature. The optimally doped sample was prepared by oxygenation of the as-prepared pellet under 120 atm at 430 °C for 22 hours. The overdoped sample required multistep pressure oxygenation with the last stage under 350 atm oxygen at 300 °C.

The phase purity of the CLBLCO samples was carefully checked by X-ray powder diffraction (XRD). Intensities were collected by a Siemens D-5000 diffractometer with  $Cu-K_{\alpha}$  radiation using the stepscan method  $(0.02^{\circ} \text{ per 8 second step})$ . For all samples all lines of the X-ray patterns could be indexed in terms of the cell constants, thus confirming that all the pellets were singlephase. Oxygen content was measured by iodometric halfmicrotitration analogous to that described in reference [2] with reproducibility 0.002. Resistivity was measured by the standard four-probe dc method on samples containing pressed indium contacts. The ac susceptibility was measured on small (20–50 mg) slices of the bar and confirmed the high oxygen homogeneity; only a single superconductive transition is observed in both  $\chi'$  and  $\chi''$ vs. T. The three samples for the high pressure studies were underdoped, optimally doped and overdoped with  $T_{\rm c}$  onsets at ambient pressure (21.6 K, 52.3 K, 26.2 K), oxygen contents y (6.991, 7.141, 7.232), approximate dimensions  $(2.4 \times 1.6 \times 1.3 \text{ mm}^3, 2.4 \times 1.1 \times 1.2 \text{ mm}^3)$  $2.0 \times 1.5 \times 1.0 \text{ mm}^3$ ), and sample masses (24.6 mg, 16.8 mg, 11.3 mg), 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 is measured by a calibrated manganin gauge and can be changed at any temperature above the melting curve of the He pressure medium. The superconducting transition of the CLBLCO sample in the high pressure environment 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 0.1 Oe (rms) at 507 Hz is applied along the long dimension of the sample. Further details of the experimental setup are given elsewhere [10].

In Figure 2 we show the real part of the ac susceptibility *versus* temperature for the optimally doped CLBLCO sample at both ambient and high pressure (0.72 GPa). The superconducting transition temperature is seen to increase rapidly with pressure. The small "dent" in the highpressure data near 50 K marks the location of the melting curve of the He pressure medium.

## **3** Results of experiment

In Figure 1 we show the dependence of the resistivity onset  $T_c$  on oxygen content y for the CLBLCO samples with x = 0.1, clearly displaying the approximate inverted

**Table 1.** Dependence of ambient-pressure  $T_c$  and pressure derivatives at both ambient (RT) and low temperatures (LT) on oxygen content y for four  $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$  samples with x = 0.1. See text for details.

source	y	$T_{\rm c}$ (1 bar) (K)	$(dT_c/dP)_{LT}$ (K/GPa)	$(dT_c/dP)_{\rm RT}$ (K/GPa)
present	6.991	21.6	$+4.31\pm0.05$	$+5.54\pm0.15$
Ref. [9]	7.068	45.4	$+4.70\pm0.15$	$+4.70\pm0.15$
present	7.141	52.3	$+5.24\pm0.04$	$+5.49\pm0.14$
present	7.232	26.2	$+5.15\pm0.08$	$+5.15\pm0.08$



Fig. 2. Real part of the ac susceptibility versus temperature for  $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$  for x = 0.1 and y =7.141 at both ambient and high pressures. Data are sufficiently dense to form a solid line. The inset shows a blowup of the onset to superconductivity to demonstrate how  $T_c$  is determined.

parabolic dependence characteristic for HTSC [3]. The three samples chosen for the present study are indicated by the open circles in this figure; the respective values of the ac susceptibility onset  $T_c$  (1 bar) and y are given above and in the Table 1. In a simple charge-transfer model, where the only effect of pressure is to increase the (hole) carrier concentration,  $T_c$  would be expected from Figure 1 to increase with pressure for the underdoped sample, remain constant for the optimally doped sample, and decrease with pressure for the overdoped sample [5]. We now compare these expectations with experiment.

#### 3.1 Underdoped sample

The results of the present high-pressure studies on the underdoped CLBLCO sample are shown in Figure 3. A pressure of 0.8 GPa was applied and held at 298 K (RT) for 30 minutes before cooling down to measure  $T_c \simeq 25.2$  K, a 3.6 K increase over the initial value of 21.6 K at ambient pressure. Due to the contraction of the helium pressure medium upon cooling, the pressure at temperatures near  $T_c$  decreased from 0.8 to 0.65 GPa, yielding the pressure derivative  $(dT_c/dP)_{\rm RT} \simeq (+3.6 \text{ K}) \div (0.65 \text{ GPa}) =$  $+5.54 \pm 0.15 \text{ K/GPa}$ . The pressure was then successively reduced to 1 bar, keeping the temperature always at low temperatures (LT) below 50 K, resulting in the  $T_c(P)$  dependence given by pts. 2 to 7 in Figure 3 with the pressure derivative  $(dT_c/dP)_{\rm LT} \simeq +4.31 \pm 0.05 \text{ K/GPa}$ . Note that



**Fig. 3.** Dependence of  $T_c$  on hydrostatic pressure in underdoped  $(\text{La}_{1-x}\text{Ca}_x)(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$  for x = 0.1 and y = 6.991. Numbers give order of measurement. Solid lines are guides to the eye.

at ambient pressure (pt. 7)  $T_{\rm c}$  has not returned to its initial value (pt. 1), but lies ~ 0.8 K above it. This is the hallmark of relaxation behavior in HTSC which presumably originates from mobile oxygen defects: that the pressure dependence of  $T_{\rm c}$  depends on the temperature at which the pressure is changed [5,6]. A measure of the magnitude of the relaxation effect in  $T_{\rm c}$  is given by the value of the derivative

$$\left(\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}P}\right)_{\mathrm{relax}} \equiv \left(\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}P}\right)_{\mathrm{RT}} - \left(\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}P}\right)_{\mathrm{LT}}.$$
 (1)

For the present underdoped sample, therefore,  $(dT_c/dP)_{relax} \simeq +1.23 \text{ K/GPa}$  which is ~30% as large as  $(dT_c/dP)_{LT}$ . The underdoped sample was then annealed at ambient pressure at 100 K for one hour, with no measurable change in  $T_c$  (pt. 8 in Fig. 3). Subsequent annealings at 200 K (pt. 9), 250 K (pt. 10) and 298 K (pt. 11) for one hour are seen to result in the full relaxation of  $T_c$  back to its initial value (pt. 1).

To investigate the observed relaxation behavior in the underdoped sample in more detail, it is desirable to study the dependence of  $T_{\rm c}$  on the time the sample is annealed at a fixed temperature following a change in pressure. To this end we applied and held a pressure of 0.61 GPa at 298 K for 2 hours before cooling down to measure  $T_{\rm c} \simeq 24.6$  K, an increase of 3.0 K over the ambient pressure value. Fully releasing the pressure at 47 K results in pt. 1 in Figure 4 with  $T_{\rm c} \simeq 22.38$  K. The relaxation of  $T_{\rm c}$  from 22.38 K



Fig. 4. Dependence of  $T_c$  on annealing time at two different temperatures following the release of pressure on the underdoped sample in Figure 3 at low temperature. Numbers give order of measurement. Solid lines are fits using equation (2).

back to 21.6 K is now studied by first heating the sample as quickly as possible (25 minutes) to 240 K and annealing at this temperature for varying lengths of time, yielding pts. 1–5 in Figure 4. To speed up the relaxation, the sample was then annealed at the higher annealing temperature of 280 K (pts. 6–10).

We now attempt to fit the data in Figure 4 using the stretched-exponent expression [11]

$$T_{\rm c}(t) = T_{\rm c}(\infty) - [T_{\rm c}(\infty) - T_{\rm c}(0)] \exp\left\{-\left(\frac{t+t_{\rm o}}{\tau}\right)^{\alpha}\right\},\tag{2}$$

where  $t_0$  is an additional time to account for possible partial relaxation occurring before t = 0 and  $\tau$  is the temperature-dependent relaxation time which is related to the activation energy barrier  $E_A$  by the Arrhenius law

$$\tau = \tau_{\rm o} \exp\left\{\frac{E_{\rm A}}{k_{\rm B}T}\right\},\tag{3}$$

where we use the value of the attempt period  $\tau_{\rm o} \approx$  $1.4 \times 10^{-12}$  s from temperature-quench experiments on YBCO [12]. Since the relaxation data at 280 K are more extensive, we fit these data first. Prior to the relaxation measurement at 280 K, some relaxation already occurred during the 13 hour anneal at 240 K which we will take into account by an additional time  $t_0$ . The final and initial transition temperatures for the 280 K relaxation data are set fixed to  $T_{\rm c}(\infty) = 21.6$  K and  $T_{\rm c}(0) = 22.38$  K. The fit to the 280 K-data in Figure 4 results in  $\tau$  (280 K)  $\simeq$ 0.51 hours,  $\alpha \simeq 0.32$  and  $t_{\rm o} \simeq 6.6$  min. Using this value of  $\tau$  (280 K), the expected value of  $t_{\rm o}$  based on the 13 hour annealing time at 240 K can be estimated. Using this value of  $t_{\rm o}$  as a fixed parameter, the fit to the 280 K-data is now repeated, yielding new values for  $\tau$  (280 K) and  $\alpha$ . Using this new value for  $\tau$  (280 K),  $t_{\rm o}$  can now be reestimated, etc. This procedure is iterated until the relaxation time from the fit is consistent with the value of  $t_{0}$  estimated, yielding  $\tau \simeq 0.31 \pm 0.04$  hours,  $\alpha \simeq 0.26 \pm 0.01$ , and  $t_{\rm o} \simeq 2.4$  minutes. Using equation (3) this corresponds to an activation energy  $E_{\rm A} \simeq 0.828 \pm 0.003$  eV.

We now check whether the parameters derived from the fit to the 280 K-data in Figure 4 are consistent with



**Fig. 5.** Dependence of  $T_c$  on hydrostatic pressure in optimally doped  $(\text{La}_{1-x}\text{Ca}_x)(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y$  for x = 0.1 and y = 7.141. Numbers give order of measurement. Solid line is guide to the eye.

the relaxation data at 240 K. Inserting  $E_{\rm A} \simeq 0.828$  eV into equation (3), we obtain  $\tau$  (240 K)  $\simeq 95.0$  hours. The best fit to the relaxation data at 240 K using this relaxation time in equation (2) yields  $T_{\rm c}(\infty) = 21.71 \pm 0.02$  K and  $\alpha \simeq 0.14 \pm 0.01$ . As seen in Figure 4, the solid lines fit the data very well. The fact that  $T_{\rm c}(\infty)$  lies at a somewhat (0.11 K) higher temperature for annealing at 240 K compared to 280 K is consistent with experiments on YBCO [12] where the lower annealing temperature results in a higher state of oxygen defect ordering which causes  $T_{\rm c}$  to shift upwards. Also, the lower value of  $\alpha$  for the 240 K-anneal is consistent with the expectation from equation (3) that the stretched exponent  $\alpha$  should become smaller as the temperature is lowered [13].

In previous work [9] we studied  $T_c(P)$  to 0.8 GPa on CLBLCO samples for several values of cation substitution x and oxygen content y, including a single sample with x = 0.1, y = 7.068 and  $T_c \simeq 45.4$  K shown as a cross in Figure 1; it is evident that this underdoped sample fits in well with the  $T_c(y)$  systematics for all samples. It is interesting to note that, unlike for the present underdoped sample,  $T_c(P)$  from the previous underdoped sample gave no evidence for relaxation behavior. Perhaps this is a result of the somewhat higher oxygen content of the latter sample. As seen in Table 1, its pressure derivative  $dT_c/dP \simeq +4.70 \pm 0.15$  K/GPa is indeed intermediate between that of the present underdoped and optimally doped samples.

### 3.2 Optimally doped sample

As seen in Figure 5, for the optimally doped CLBLCO sample a pressure of 0.8 GPa was applied and held at 298 K for 30 minutes before cooling down to measure  $T_{\rm c} \simeq 56.3$  K, a value 4.0 K above the initial value of 52.3 K at ambient pressure. At temperatures near  $T_{\rm c}$  the pressure had decreased to 0.72 GPa. The pressure was then successively decreased at temperatures below 50 K and  $T_{\rm c}$  remeasured each time (pts. 2–7 in Fig. 5), yielding a linear  $T_{\rm c}(P)$ -dependence with slope  $({\rm d}T_{\rm c}/{\rm d}P)_{\rm LT} \simeq +5.24 \pm 0.04$  K/GPa. After full release of pressure (pt. 7),  $T_{\rm c} \simeq 52.5$  K which equals the initial value of 52.3 K (pt. 1) within experimental error



Fig. 6. Dependence of  $T_c$  on hydrostatic pressure in overdoped  $(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$  for x = 0.1 and y = 7.232. Numbers give order of measurement. Solid line is guide to the eye.

(±0.1 K). After annealing the sample for 1 h at 298 K (pt. 8),  $T_c$  appears to shift downward slightly to coincide with the initial value. Further experiments to even higher precision would be necessary to ascertain whether or not there is any relaxation behavior in  $T_c$  for this sample; in any case, the effect must be very small. One would not expect any relaxation which might occur in this sample to change  $T_c$  since this sample is optimally doped. Oxygen ordering processes are believed to primarily result in charge transfer to and from the CuO<sub>2</sub> plane(s); a charge transfer alone would not change  $T_c$  in an optimally doped sample where  $T_c(n)$  is at an extremum with respect to the carrier concentration n [5,6].

## 3.3 Overdoped sample

The overdoped CLBLCO sample was subjected to 0.8 GPa pressure at 298 K and held at that temperature for 30 minutes before cooling to low temperatures to measure  $T_{\rm c} \simeq$ 29.6 K (pt. 2 in Fig. 6), a temperature 2.6 K higher than the initial value at ambient pressure (26.2 K). Additional annealing at 298 K for two more hours did not cause any further change in the transition temperature. The pressure was then decreased at 55 K to 0.53 GPa (pt. 3) and then fully released (pt. 4);  $T_{\rm c}$  is seen to vary linearly and to revert to its initial value at ambient pressure. Applying and holding 0.46 GPa pressure for 1 h at 298 K results in pt. 5 in Figure 6. Further releasing the pressure to 0.21 GPa at 43 K yields pt. 6; annealing the sample then at 298 K (0.25 GPa) for 16 h (pt. 7) caused no further change in  $T_{\rm c}$ . Finally, fully releasing the pressure at 41 K (pt. 8) yields the initial value at ambient pressure (26.2 K). Since the dependence of  $T_{\rm c}$  on pressure,  $(dT_c/dP) \simeq +5.15 \pm 0.08 \text{ K/GPa}$ , is independent of the pressure/temperature history of the sample, we find no evidence for relaxation behavior in this overdoped sample, *i.e.*  $(dT_c/dP)_{relax} \simeq 0$ . The results of the above experiments are summarized in Table 1.

# 4 Discussion

For all three samples studied in these experiments, as well as for all CLBLCO samples studied in our previous work [9],  $T_c$  is found to increase linearly with pressure to 0.8 GPa whether the pressure is changed at low or ambient temperatures. It thus is likely that there are no pressure-induced structural phase transitions in CLBLCO over the present pressure and temperature regions, in contrast to overdoped Hg-1201 where  $dT_c/dP$  was found to change markedly near 0.4 GPa [14].

In CLBLCO weak pressure-induced relaxation effects in  $T_{\rm c}$  have only been observed for one of the two underdoped samples with x = 0.1 (see Tab. 1) and in two underdoped samples with x = 0.2 from a previous study [9]. In contrast, relatively strong relaxation effects have been found for YBCO across the entire range of oxygen doping, particularly for the most underdoped samples where values as large as  $(dT_c/dP)_{relax} \approx +20 \text{ K/GPa}$  have been observed, a value ten times as large as  $(dT_c/dP)_{LT}$ for the same sample [7]! We speculate that the relative scarcity and weakness of the relaxation effects in CLBLCO may be due either to the enhanced disorder in the system from the extensive cation substitution or to the lack of the chain structure in this tetragonal system. Further studies on CLBLCO over a wider range of oxygen content (see Fig. 1) and a higher degree of cation substitution x are required to gain a clear picture of the role of relaxation phenomena in this system.

To search for systematics in high-pressure data on HTSC for comparison to theoretical models, it is desirable to determine the pure dependence of  $T_c$  (and other properties) on pressure under experimental conditions where relaxation phenomena and other structural changes have been suppressed. As discussed above, the linearity of the  $T_c(P)$  data speaks against the occurrence of structural phase transitions in the present pressure/temperature range. As we learned from Figure 3, relaxation effects can be suppressed by changing the pressure at temperatures at or below 100 K, a result which also holds for YBCO [15]. In the following we will restrict ourselves to a discussion of the pressure derivative  $(dT_c/dP)_{\rm LT}$  at temperatures sufficiently low to freeze out relaxation processes.

As seen in Table 1, for all four CLBLCO samples with x = 0.1 studied, the pressure derivative  $(dT_c/dP)_{LT}$ takes on surprisingly large, positive values,  $(dT_c/dP)_{LT} \approx$ +5 K/GPa, which increase somewhat from the underdoped to the optimally doped, and decrease only slightly to the overdoped side. Underdoped samples of YBCO exhibit comparable values of  $(dT_c/dP)_{LT}$ , but a much smaller value for nearly optimally doped YBCO [7]. Neumeier and Zimmermann [16] have estimated that for optimally doped YBCO  $(dT_c/dP)_{LT} \approx +1$  K/GPa. This estimate was based on a successful analysis of highpressure data on a series of cation substituted YBCO compounds in terms of a modified charge-transfer model which breaks the total pure pressure derivative of  $T_c$  up into two parts:

$$\left(\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}P}\right)_{\mathrm{LT}} = \left(\frac{\partial T_{\mathrm{c}}}{\partial n}\right) \left(\frac{\partial n}{\partial P}\right) + \left(\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}P}\right)_{\mathrm{intrinsic}}.$$
 (4)

The first part takes into account the normal transfer of hole charge n into the CuO<sub>2</sub> plane(s) with increasing pressure [4,5], *i.e.* dn/dP is a positive quantity, and the second part gives the so-called "intrinsic" pressure dependence of  $T_{\rm c}$  which arises from changes in basic quantities like the density of electron states or the coupling parameter. If the "intrinsic" dependence is negligible, then  $T_{\rm c}$  would be expected from equation (4) and Figure 1 to increase under pressure for underdoped samples where  $dT_c/dn > 0$ , remain constant for optimally doping  $(dT_c/dn = 0)$  and decrease for overdoped samples  $(dT_c/dn < 0)$ . If  $(dT_c/dP)_{intrinsic}$  is not negligible, then from equation (4) one would still expect, if the chargetransfer term  $\partial n/\partial P$  in equation (4) is important and reasonably constant, that the measured value of  $(dT_c/dP)_{LT}$ would tend to become less positive or more negative going from underdoped to optimally doped to overdoped samples. That this is not at all the case in the present experiments on CLBLCO indicates that pressure-induced charge-transfer effects play only a secondary role. We conclude that the values of  $(dT_c/dP)_{LT}$  for the under- to overdoped samples in Table 1, which are uniformly large and positive, reflect primarily the intrinsic dependence of  $T_{\rm c}$  on pressure and point to a common cause for the pressureinduced changes in the superconductivity over the entire underdoped to overdoped region.

It is interesting to note that a similar result was obtained previously for  $La_{2-x}Sr_xCuO_4$  [17], another system with a relatively low value of  $T_{\rm c}$  at optimal doping and negligible charge transfer under pressure [5]. The large magnitude of  $dT_c/dP \approx +5$  K/GPa in optimally doped CLBLCO relative to YBCO (+1 K/GPa) may be related to the fact that the latter system possesses a much higher value of  $T_{\rm c}$  at optimal doping, namely 92 K compared to 57 K in CLBLCO for x = 0.1 (see Fig. 1). In CLBLCO for x = 0.4 the transition temperature takes on a higher value near 80 K at optimal doping [4]; for this sample  $(dT_c/dP)_{LT} \approx +1-2 \text{ K/GPa}$ , a value much closer to that for optimally doped YBCO. It is interesting to note that the degree of buckling at optimal doping is greater for the CLBLCO system with x = 0.1 than for x = 0.4 which may be related to the higher value of  $T_{\rm c}$  for the latter. We thus speculate that the ubiquitous increase of  $T_{\rm c}$  with pressure in CLBLCO may be caused by a decrease in the degree of buckling, a possibility that should be checked in future structural studies under high-pressure conditions.

On a more general note, we point out that, as for the Hg-compounds, nearly ideal optimally doped oxide superconductors with one, two and three (CuO<sub>2</sub>) planes appear to exhibit transition temperatures near 95 K, 120 K and 135 K, respectively. If a particular optimally doped system exhibits a lower value of  $T_c$ , this may indicate the presence of structural defects of various kinds, such as buckled planes [18]. If the application of pressure were to significantly reduce the effects of these defects, then  $T_c$  would be expected to increase particularly rapidly. It is interesting to note that for nearly optimally doped cuprate superconductors an inverse correlation appears to exist between the magnitude of  $T_c$  and that of its pressure derivative  $dT_c/dP$  [5]. The work at Washington University is supported by the National Science Foundation under grant DMR 98-03820. The work in Israel is supported by the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities and by the Center of Absorption in Science, Ministry of Immigrant Absorption, Israel.

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