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# Pressure dependence of $T_c$ in cuprate superconductors: Application to $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$

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We have measured the pressure dependence of the superconducting transition temperature $T_c$ within a large range of doping in $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$. This charge-compensated 1:2:3 family is tetragonal, and free of the plateau structure and of structural phase transitions. The pressure $(P)$ dependence of $T_c$ is analyzed in terms of two easily determined variables, $T_c^{\max}$ (maximal attainable $T_c$) and the relative chemical charge $\Delta q = y - y_{\text{M-I}}(x)$ (the oxygen content $y$ measured with respect to its value at the metal-insulator transition), used to describe the dependence of $T_c$ on doping for all values of $x$ and $y$. Assuming a simple parabolic relationship between $T_c$ and $\Delta q$ that does not broaden with $P$, we derive an expression for $dT_c/dP$ containing contributions from both $d\Delta q/dP$ and $dT_c^{\max}/dP$ which are dominant far away from and in the vicinity of optimal doping, respectively. We obtain in this family reliable values of the derivatives, $dT_c^{\max}/dP = +1.7$ K/GPa and $d\Delta q/dP = +0.011|e|$/GPa which are *constant, independent of the doping level,* as anticipated by our simple analysis.

## I. INTRODUCTION

The pressure dependence of the transition temperature $T_c$ of cuprate superconductors has been the subject of intensive research in recent years.[1] Guided by the idea of replacing external pressure by internal ''chemical pressure'' in an attempt at yielding higher $T_c$,[2] or searching for a clue to the underlying mechanism,[1] measurements under pressure have been one of the major tools in the investigation of new materials. It was found that in many cuprates the pressure $(P)$ derivative $dT_c/dP$ is large and positive in the so-called underdoped regime, decreasing towards optimal doping and eventually becoming negative in the strongly overdoped regime. It has been suggested by Hall effect and neutron-diffraction studies[1,3] that the effect of pressure on $T_c$ arises in part from electron transfer from the $\mathrm{CuO}_2$ planes to the charge reservoir, thereby increasing the mobile hole density $n_h$ per $\mathrm{CuO}_2$ plane. However, attempts at a quantitative analysis of the dependence of $T_c$ on pressure, based solely on the pressure-induced charge-transfer model, have not been particularly successful, suggesting that additional variables might be important.[1,4]

The variables that would best describe the pressure dependence of $T_c$ can be found in the variables that are used in the description of $T_c$ itself. At least *two* independent variables are needed to describe $T_c$. One obvious choice of such a variable would be a parameter that describes the dependence of $T_c$ on doping. It is well known in cuprates that by means of chemical changes it is possible to vary $T_c$ smoothly and in a systematic manner within the underdoped, optimally doped or overdoped regimes. Such chemical changes are believed to alter the mobile hole density $\Delta n_h$ (measured with respect to optimal doping). The work of Obertelli, Cooper, and Tallon[5] and of Zhang and Sato[6] suggests that $T_c^{\max}$ should be the second variable. $T_c^{\max}$ denotes the value of $T_c$ at optimal doping, that is, the maximal value of $T_c$ within a material family attainable by doping at a given pressure. Both $\Delta n_h$ and $T_c^{\max}$ would then be expected to be pressure dependent. The importance of using two independent variables in the investigation of $dT_c/dP$ has already been recognized in the early work by van Eenige (vE) *et al.*[7] These authors investigated $dT_c/dP$ in $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_y$ (YBCO) as function of pressure at various values of oxygen content $y$. In their model they use the doping variable $\Delta n_h$ and the other variable that they use is related to $T_c^{\max}$. The use of two variables in the determination of $dT_c/dP$ may allow one to understand why in slightly overdoped materials $dT_c/dP$ remains positive. Were $T_c$ solely a function of $\Delta n_h$, $dT_c/dP$ should be identically zero at optimal doping, becoming positive or negative for underdoping or overdoping, respectively.[1,4]

More recently, this work was extended by two other investigations on pure YBCO and on Ca- or La-substituted YBCO by Almasan *et al.*[8] and by Neumeier and Zimmermann (NZ).[4] Following vE *et al.* these authors use the same variables $\Delta n_h$ (again referred to full stoichiometry) and $T_c^{\max}$ for describing $T_c$. In both investigations $\Delta n_h$ was taken to be the microscopic mobile hole density in the $\mathrm{CuO}_2$ planes, as in the work of vE *et al.* However, Almasan *et al.* obtain this parameter from bond-valence-sums arguments while NZ use for this quantity the concentration of substituted atoms which, they believe, represents the mobile hole density.

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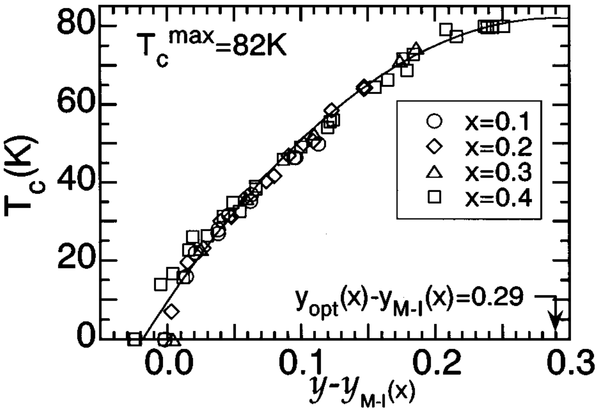

FIG. 1. Parabolic relation between $T_c$ (resistive onset) and $y-y_{\text{M-I}}(x)$ for various compositions $x$ and oxygen contents $y$. This curve was taken from Ref. 10.

Our method of analyzing $dT_c/dP$, described in Sec. II, does not depend on a particular choice of variables. However, there are variables that make the analysis and in particular the interpretation more straightforward. Thus use of $\Delta n_h$ was avoided because it is not a directly observed quantity.

Recently, we have investigated the new family of 1:2:3 materials $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$, (CaLaBaCuO) obtained by charge-compensating cosubstitution in the same amount of $\mathrm{Ca}^{2+}$ on the $\mathrm{Y}^{3+}$ site (first bracket) and of $\mathrm{La}^{3+}$ on the $\mathrm{Ba}^{2+}$ site (second bracket).[9] For all values of $x$ and $y$ these materials have a tetragonal structure, thereby avoiding long-range oxygen order. At any given composition $x$, the dependence of $T_c$ on oxygen content $y$ in the underdoped regime can be approximated closely by a parabolic relation, that is, no plateau structure was observed. Moreover, for all values of $x$ and $y$ the dependence of $T_c$ on the doping level can be described in terms of a single macroscopic parameter $y-y_{\text{M-I}}(x)$.[10] $y_{\text{M-I}}$, which is a function of the compositional parameter $x$, denotes the value of $y$ at the metal-insulator (M-I) transition which was identified with $T_c \rightarrow 0$ K. These observations are summarized in Fig. 1 where we have plotted $T_c$ as function of $y-y_{\text{M-I}}(x)$ for various values of $x$. The curves that describe the dependence of $T_c$ on $y$ for each value of $x$, all coalesce into a single curve when plotted as function of $y-y_{\text{M-I}}(x)$. A similar coalescence of the curves was observed in the dependence of resistivity and thermoelectric power on $y-y_{\text{M-I}}(x)$.[10] In other words, the doping is determined not only by the oxygen content $y$, but also by the dependence of $y_{\text{M-I}}$ on $x$, which must be determined in a separate experiment. We assume that the same $T_c^{\max}$ holds for all values of $x$. This is supported by our observation that $T_c$ is a unique function of $y-y_{\text{M-I}}(x)$ and by assuming that the universal curve suggested by Obertelli *et al.*[5] (i.e., the thermoelectric power is a universal function of $T_c/T_c^{\max}$) is valid also for CaLaBaCuO. Also notice in Fig. 1 that one could use $y-y_{\text{opt}}(x)$ instead of $y-y_{\text{M-I}}(x)$ to describe the doping dependence of $T_c$ [$y_{\text{opt}}(x)$ is the oxygen content where $T_c$ should reach its maximal value]. Clearly this is the case for $x=0.4$ when $y_{\text{opt}}-y_{\text{M-I}}=0.29$. This then allows one to use a simple expression for the parabolic dependence of $T_c$ on $y$.

## II. ANALYSIS OF THE DEPENDENCE OF $dT_c/dP$ ON DOPING

We would now like to derive an expression for $T_c$ in terms of macroscopic variables that can be determined unambiguously from experiment. Following our work on CaLaBaCuO, we choose the variables $T_c^{\max}$ and the relative chemical charge $\Delta q = y - y_{\text{opt}}$. (More generally one could define $\Delta q = q - q_{\text{opt}}$, where $q$ denotes the chemical charge contributed *either* by anions *or* by cations; see Sec. V). We prefer the use of $\Delta q$, rather than the actual doping level $\Delta n_h$. The former is a directly observable quantity whereas the latter is subject to uncertainties arising from an unknown amount of hole splitting between mobile and localized (e.g., charge reservoir) states. Notice that $n_h$ changes with pressure. This problem is avoided when the chemical charge $q$ is used which, unlike $n_h$, does not change with pressure. For simplicity, we have ignored any proportionality constant in the definition of $\Delta q$, e.g., $\Delta q = 2(y - y_{\text{opt}})$ that might be expected since a change in oxygen content $y$ by one atom changes $q$ by two electron charges. Such proportionality constants would only affect the value of the constant $C$ [Eq. (3)].

To proceed, we now postulate that $T_c$ is an explicit function of the two independent variables $T_c^{\max}$ and $\Delta q$ alone, i.e., $T_c = T_c(T_c^{\max}, \Delta q)$. Hence

$$dT_c = \left(\frac{\partial T_c}{\partial T_c^{\max}}\right)_{\Delta q} dT_c^{\max} + \left(\frac{\partial T_c}{\partial \Delta q}\right)_{T_c^{\max}} d\Delta q. \tag{1}$$

The pressure dependence enters through $T_c^{\max}$ and $q_{\text{opt}}$.

Upon application of an incremental pressure $dP$ to a sample with a given $y$ (or $q$), the full derivative of $T_c$ with respect to $P$ is obtained directly from Eq. (1):

$$\left(\frac{dT_c}{dP}\right)_q = \left(\frac{\partial T_c}{\partial T_c^{\max}}\right)_{\Delta q} \left(\frac{dT_c^{\max}}{dP}\right)_q + \left(\frac{\partial T_c}{\partial \Delta q}\right)_{T_c^{\max}} \left(\frac{d\Delta q}{dP}\right)_q. \tag{2}$$

Notice that both $(dT_c^{\max}/dP)_q$ and $(d\Delta q/dP)_q$ are independent of $q$, taking on a constant value at a given pressure, independent of the chemical charge or doping level. In particular, $(d\Delta q/dP)_q = -dq_{\text{opt}}/dP$ is independent of $q$, as it describes the behavior of some specific charge (i.e., $q_{\text{opt}}$) under pressure. We take the derivative at constant $q$ (or constant $y$) because the measurements are done on one sample at a time, that is, $q$ remains constant when $dT_c/dP$ is measured. This is an important aspect of our analysis. Had we chosen $\Delta n_h$ instead of $\Delta q$,[4,8] $(d\Delta n_h/dP)_q$ would contain the term $(dn_h/dP)_q$ that depends on $q$ and therefore would not be constant at various doping levels. This approach clearly simplifies the analysis.

We proceed by assuming a parabolic ''equation of state'' between $T_c$ and $q$ of the form

$$T_c = T_c^{\max}[1 - C(\Delta q)^2]. \tag{3}$$

Apart from a small deviation near $y_{\text{M-I}}$, this form holds in CaLaBaCuO at ambient pressure as our measurements show (see Fig. 1). In other materials the value of $C$ in Eq. (3) will depend on the actual compositional parameter chosen to de-

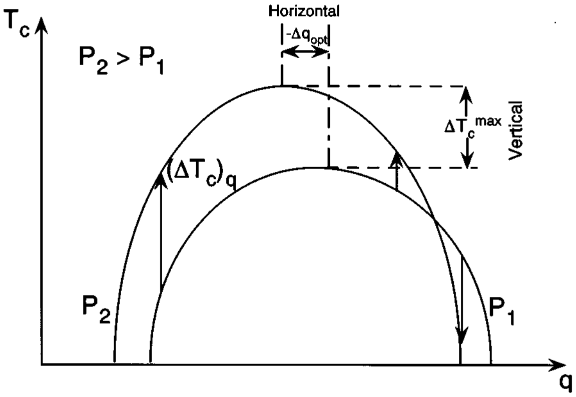

FIG. 2. Schematic presentation of the quadratic dependence of $T_c$ on the chemical charge $q$ at two different pressures. Vertical arrows indicate change in $T_c$ of a given sample having a specific value of $q$ (i.e., of the doping level).

scribe $\Delta q$. The partial derivatives of Eq. (2) are then easily obtained from Eq. (3), yielding

$$\left(\frac{dT_c}{dP}\right)_q = \frac{T_c}{T_c^{\max}}\left(\frac{dT_c^{\max}}{dP}\right)_q - 2CT_c^{\max}\Delta q\left(\frac{d\Delta q}{dP}\right)_q, \tag{4}$$

where $C$ is assumed to be independent of pressure (see below). Equation (4) can be rewritten in a linear form as

$$\frac{T_c^{\max}}{T_c}\frac{dT_c}{dP} = \frac{dT_c^{\max}}{dP} + 2CT_c^{\max}\frac{d\Delta q}{dP}\left[-\Delta q\frac{T_c^{\max}}{T_c}\right]. \tag{5}$$

This equation is linear with respect to the term in the bracket on the right-hand side (rhs) only because $dT_c^{\max}/dP$ and $d\Delta q/dP$ are constants independent of the doping level. In this way one can extract a reliable value of the fundamental quantity $dT_c^{\max}/dP$. This is done by plotting the left-hand side of Eq. (5) vs the variable in square brackets on the rhs of Eq. (5). Strictly speaking, we know the dependence $T_c(T_c^{\max},\Delta q)$ only at ambient pressure. Therefore, the values of $dT_c^{\max}/dP$ and $d\Delta q/dP$ that we obtain in this work hold only at ambient pressure.

Notice in these equations that $\Delta q$ is negative for underdoped and positive for overdoped samples, respectively. $d\Delta q/dP$ represents a ''horizontal'' shift of the center of the parabola in Eq. (3), as can be seen in Fig. 2. $dT_c^{\max}/dP$ denotes an additional ''vertical'' pressure dependence of the parabola. It often happens that the term with $dT_c^{\max}/dP$ is the dominant term in the dependence of $T_c$ on $P$. In fact, a large value of the prefactor $\Delta q$ or $T_c/T_c^{\max}$ in Eq. (4), makes the terms containing $d\Delta q/dP$ or $dT_c^{\max}/dP$ dominant far away from, or in the vicinity of optimal doping, respectively. Hence, consideration of pressure-induced charge transfer as the only or major pressure effect is only appropriate well away from optimal doping.

We ignored in the above derivation any possible pressure dependence of $C$. This can be justified *a posteriori* on experimental grounds. The confirmation of this constant-$C$ assumption, as well as the applicability of the parabolic relationship in Eq. (3), is the experimentally observed linear dependence of $(T_c^{\max}/T_c)(dT_c/dP)$ on $\Delta q(T_c^{\max}/T_c)$, in accordance with Eq. (5). Moreover, assuming an explicit dependence of $C$ on $P$ would disrupt the linear relationship via addition of the slowly varying partial logarithmic derivatives $(\partial \ln C/\partial T_c^{\max})_{\Delta q}$ and $(\partial \ln C/\partial \Delta q)_{T_c^{\max}}$ on the rhs of Eq. (5) that multiply $(dT_c^{\max}/dP)_q$ and $(d\Delta q/dP)_q$, respectively. Far away from optimal doping these contributions disrupt linearity as both logarithmic derivatives are multiplied also by $(T_c^{\max}-T_c)$. Notice that the appearance of the term $T_c/T_c^{\max}$ in Eq. (4) and of its inverse in Eq. (5) is a direct consequence of taking $C$ independent of pressure.

## III. EXPERIMENT

Sample preparation has been described in detail elsewhere.[9] Essentially we used solid-state reaction procedure followed by slow oxidation to yield the mostly oxidized material ($y=7.15$ at $x=0.4$). Reduction and quench to liquid nitrogen was done in a vertical furnace containing dry $O_2$ or $N_2$ atmosphere. All samples are composed of high purity and oxygen homogeneous single phase material containing no traces of impurity phases. The materials have the tetragonal 1:2:3 structure for all samples used in the present work. Details on the sample composition and oxygen content are given in Table I. All measurements including $T_c, dT_c/dP$ and oxygen content have been performed on a single sample. Accurate determination of the oxygen content within a sample has been achieved by microtitration on three pieces

TABLE I. Data on CaLaBaCuO samples used in Fig. 4. All compositions have the same $T_c^{\max}$. All samples except 11 are of composition $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$. Sample 11, which is slightly overdoped has the composition $(Ca_{0.4}La_{0.6})(Ba_{1.6}La_{0.4})Cu_3O_y$.

| No. | $x$ | $y_{\text{M-I}}$ | $y$ | $-\Delta q$[a] | $T_c$ K | $-\Delta q(T_c^{\max}/T_c)$ | $T_{\text{He}}$[b] K | $dT_c/dP$ K/GPa | $dT_c/dP\ (T_c^{\max}/T_c)$ K/GPa |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.4 | 6.900 | 7.143 | 0.047 | 79.1 | 0.0487 | 60 | 2.10±0.10 | 2.177 |
| 2 | 0.4 | 6.900 | 7.079 | 0.111 | 74.4 | 0.1223 | 60 | 3.70±0.15 | 4.078 |
| 3 | 0.1 | 6.972 | 7.068 | 0.194 | 45.4 | 0.3504 | 60 | 4.70±0.15 | 8.489 |
| 4 | 0.2 | 6.961 | 7.084 | 0.167 | 54.0 | 0.2536 | 90 | 4.70±0.13 | 7.137 |
| 6 | 0.2 | 6.961 | 7.009 | 0.242 | 28.1 | 0.7062 | 60 | 4.60±0.20 | 13.423 |
| 9 | 0.2 | 6.961 | 6.976 | 0.275 | 15.0 | 1.5033 | 90 | 5.60±0.50 | 30.613 |
| 11 | 0.4 | 6.660 | 6.992 | -0.042 | 79.4 | -0.0434 | 90 | 1.37±0.10 | 1.415 |

[a] $-\Delta q = 0.29-(y-y_{\text{M-I}})$.

[b] Temperature at which pressure was changed during each measurement.

each with ~5 mg mass.[11] Except for sample 11, all samples in Table I have the composition $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$. For these compositions we have determined $y_{\text{M-I}}(x)$ experimentally using a procedure as described in a separate publication.[12] For sample 11, which has the composition $(Ca_{0.4}La_{0.6})(Ba_{1.6}La_{0.4})Cu_3O_y$ and is slightly overdoped, we used an extrapolation formula to determine $y_{\text{M-I}}$.[12] (This will not limit the accuracy of our results which is limited by other parameters.) In this way $y-y_{\text{M-I}}$ is fully determined and one obtains $\Delta q=y-y_{\text{opt}}$ by subtracting $y_{\text{opt}}-y_{\text{M-I}}=0.29$ from the value of $y-y_{\text{M-I}}$ (see Introduction and Fig. 1).

The pressure measurements have been carried out in a He gas pressure system at Washington University, St. Louis. Such a pressure system provides a hydrostatic pressure environment at all pressures and temperatures in this investigation.[13] We used the pressure range $P\leqslant 0.8$ GPa in which we raised and decreased the pressure several times during each measurement of $dT_c/dP$ in order to check for hysteresis effects. At each pressure, $T_c$—as determined through an ac susceptibility measurement using a field of 0.03 to 0.1 Oe— was monitored via a slow temperature ramp. The data points at various pressures fall on a straight line with only minimal scatter (see Sec. IV).

Pressure-induced oxygen ordering effects have been found to have a sizeable effect on the measured values of $dT_c/dP$ in $Tl_2Ba_2CuO_{6+y}$ and to a lesser extent in YBCO systems,[14,15] where $dT_c/dP$ depends senstivitely on the temperature at which the pressure is changed. To test for such phenomena in the present experiments, the pressure was changed at both low (60–90 K) and high (room temperature, RT) temperatures. Only for samples 6 and 9 was any difference in $dT_c/dP$ observed. These samples lie closest to the M-I transition. For sample 6 we find $(dT_c/dP)_{60\text{K}}\simeq+(4.6\pm0.2)$ K/GPa, while $(dT_c/dP)_{\text{RT}}\simeq+(5.6\pm0.2)$ K/GPa and for sample 9, $(dT_c/dP)_{90\text{K}}\simeq+(5.6\pm0.3)$ K/GPa, while $(dT_c/dP)_{\text{RT}}\simeq+(7.8\pm0.3)$ K/GPa. In Table I we give the low temperature (LT) ($T_{\text{He}}$) at which the pressure was changed during each of the $T_c(P)$ measurements. The possible influence of oxygen ordering is minimized by changing the pressure at low temperatures.

## IV. RESULTS

In Fig. 1 we present the ambient pressure results of $T_c$ vs $y-y_{\text{M-I}}(x)$ in $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ with $x=0.1,0.2,0.3,0.4$. This figure contains many samples; only a few of these samples were studied in the high-pressure measurements. The dependence of $T_c$ on $y-y_{\text{M-I}}$ is almost parabolic (see curve fit in the figure), the main deviation occurring very close to the M-I transition where the slope of the curve increases sharply. We did not use these points in the fit. The parameters that we extracted by fitting to Eq. (3) are $T_c^{\max}=82$ K, and $C=10.5|e|^{-2}$.

In Fig. 3 we show some typical results of the ac susceptibility as function of temperature at various applied pressures. Only the real part of the susceptibility ($\chi'$) is shown. The transition is narrow and does not broaden upon application of pressure. The inset in Fig. 3 is a blowup of the same measurements used to extract $T_c$. The narrow transition and the flat $\chi'$ curve below the transition are indications for homogeneously oxygenated grain boundaries in our samples.[9] In Fig. 4 we present the dependence of $T_c$ on $P$ in each of our samples (the curve for sample 11 falls close to that of sample 1 and has been removed from the figure for clarity). The fit to a linear dependence is very good in all samples.

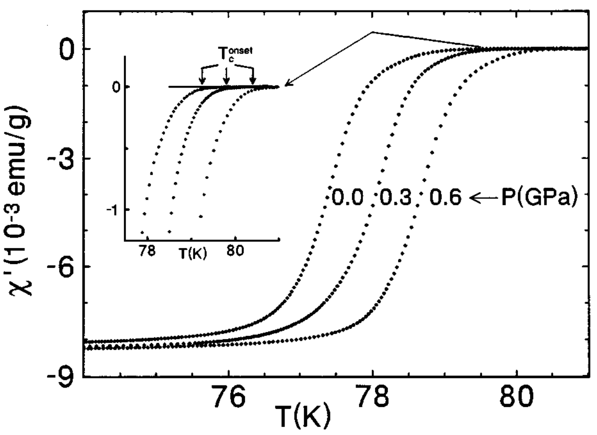

FIG. 3. Real part of the ac susceptibility (field 0.1 Oe at 507 Hz) for sample No. 1 at various pressures, yielding $dT_c/dP\simeq+2.1\pm0.1$ K/GPA.

Figure 5 presents a plot of $dT_c/dP$ vs $\Delta q$ both multiplied by the scale factor $T_c^{\max}/T_c$ according to Eq. (5). The linear fit to the results is very good over a wide range of doping in accordance with our analysis in Sec. II. There is almost no scatter in our results. This can be attributed to the good oxygen homogeneity in our samples, to an accurate determination of oxygen content, and to the high precision of the pressure measurements. The history of this experiment might be of interest. Initially, we measured only three samples (1, 2, and 3) which obeyed the linear relation [Eq. (5)]. As these points span only a small fraction of the underdoped region

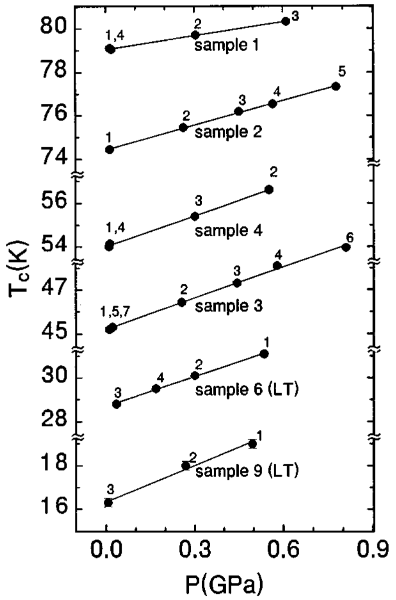

FIG. 4. Pressure dependence of $T_c$ in our samples. LT denotes samples in which $dT_c/dP$ depends on the temperature at which pressure was changed (see Table I).

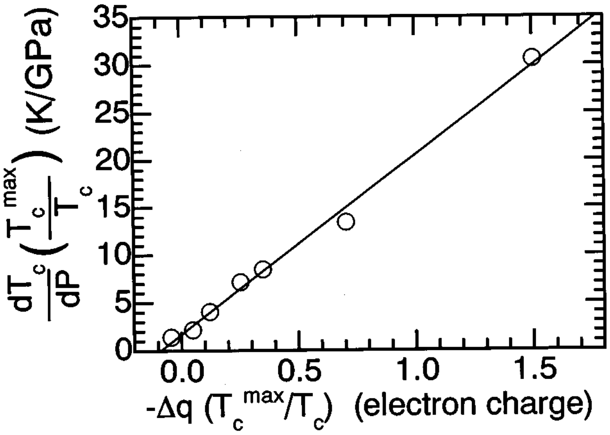

FIG. 5. The dependence of the weighted pressure derivative of $T_c$ on the weighted relative chemical charge $\Delta q$ in $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ [see Eq. (5)]. The intercept denotes $dT_c^{max}/dP = +1.7$ K/GPa. The slope yields $d\Delta q/dP = +0.011|e|$/GPa.

close to optimal doping, we used these results and a simple linear extrapolation to make predictions on the anticipated $dT_c/dP$ at other doping levels that lie further away from optimal doping. We then extended our measurements to the entire underdoped regime and our predictions turned out to be very accurate. Therefore, we believe that our procedure can be used to extrapolate values of $dT_c/dP$ in these and other materials. The linear fit is described in units of K/GPa by $(T_c^{max}/T_c)(dT_c/dP) = 1.7 - 19[\Delta q(T_c^{max}/T_c)]$ from which we obtain according to Eq. (5): $dT_c^{max}/dP = +1.7 \pm 0.2$ K/GPa and $d\Delta q/dP = +0.011 \pm 0.0005|e|$/GPA.

## V. DISCUSSION

The linearity of $(T_c^{max}/T_c)$ $(dT_c/dP)$ versus $\Delta q(T_c^{max}/T_c)$ [Eq. (5)] in CaLaBaCuO over almost the *entire underdoping regime* is very good. This linearity allows one to find the values of both $d\Delta q/dP$ (i.e., of $dy_{opt}/dP$ or $dy_{M\text{-}I}/dP$) and $dT_c^{max}/dP$ quite accurately. In fact the accuracy of $d\Delta q/dP$ is high as the slope parameter is not sensitive to the error in each measurement. The accuracy of $dT_c^{max}/dP$ is somewhat lower. In part this lower accuracy is related to the scale factor $T_c^{max}/T_c$ that multiplies $dT_c/dP$ on the ordinate of Fig. 5. The intercept, at which $dT_c^{max}/dP$ is determined (and where $T_c^{max}/T_c = 1$), represents only about 5% of full scale and is therefore sensitive to errors in $dT_c/dP$, in particular to the 5% error in $dT_c/dP$ of point No. 9. (See Table I.) The accuracy could be improved if more measurements, particularly in the overdoped regime, become available. The good linear fit over the entire underdoped regime suggests that our assumptions, e.g., the parabolicity of the ''equation of state'' [Eq. (3)] and the constancy of the width parameter $C$, are valid in CaLaBaCuO. In particular, there is no sign of any pressure dependence of $C$ that would manifest itself as a deviation from linear dependence far away from optimal doping (see Sec. II). The CaLaBaCuO family would appear to be a good prototype of the 1:2:3 system: it is tetragonal, contains no ordered chains and is free of structural phase transitions. In short, it is simpler than YBCO. The possibility of pressure dependence of the parameter $C$ deserves further study in other cuprate systems, e.g., by measurement of the dependence of $T_c$ on carrier density in the entire underdoping and overdoping regimes at different pressures.

$dT_c^{max}/dP$, which is quite large in CaLaBaCuO (i.e., +1.7 K/GPa as compared to +1.0 K/GPa in YBCO-related materials[4]), is an important quantity that should be considered in any theory of the superconducting mechanism. As it measures the increase with pressure of the highest $T_c$ within a given family, it is probably related to the pairing (rather than to carrier density). Actually, when compared with theory one frequently uses the more fundamental volumetric derivative $(dT_c^{max}/d\ln v) = (1/\kappa)(dT_c^{max}/dP)$ [or $d\ln T_c^{max}/d\ln v = (1/\kappa)(d\ln T_c^{max}/dP)$], where $\kappa$ is the volumetric compressibility and $v$ is the specific volume.[16] Thus a meaningful comparison could be made only once the compressibility of CaLaBaCuO has been measured. We note, however, that according to a model calculation by Cornelius *et al.*[17] the compressibilities of CaLaBaCuO and YBCO should be the same. In that case, the volumetric derivatives are quite different in both materials.

The interpretation of $d\Delta q/dP$ in terms of the actual (microscopic) dependence of the doping level on pressure is not straightforward. If $s$ denotes the degree of hole splitting between mobile and localized states, then the mobile hole concentration $\Delta n_h$ can be expressed as $\Delta n_h = s\cdot\Delta q$, where $\Delta q$ is the relative chemical charge. Notice that $s$ is probably a function of the doping level.[10,12] As both $n_{h,\mathrm{opt}}$ and $s$ are expected to change with pressure, it is not clear *a priori* what the dependence of $n_h$ on pressure would be.

Our method of calculation can be easily extended to other materials. As an example, consider the YBCO-related material family investigated by NZ,[4] namely, $(Ca_zY_{1-z})Ba_2Cu_3O_{6.96}$ and $Y(Ba_{2-x}La_x)$ $Cu_3O_{6.96}$, [Y(Ca)Ba(La)CuO]. Here we used $\Delta q = z - x + 0.07$, and analyze their data according to Eq. (5) using the values $C = 6.26|e|^{-2}$ and $T_c^{max} = 94.2$ K that were obtained from the analysis in Ref. 4. We obtain $dT_c^{max}/dP = +1.0$ K/GPa and $d\Delta q/dP = +0.011|e|$/GPa. These values are close to those obtained by NZ who applied a different analysis to their data. This probably reflects the relatively narrow doping range near optimal doping that was investigated in that study (i.e., $T_c/T_c^{max} \geqslant \sim 0.9$ for all samples used by NZ), in which case both analyzes become indistinguishable.

In short, the definition of $\Delta q$ in terms of composition is simple whenever one of the charge sources remains constant, as in charge-compensated cation cosubstitution[9,10,12] (e.g., CaLaBaCuO) where the definition $\Delta q = y - y_{opt}(x)$ could be used, or when the oxygen charge reservoir is held constant in which case the relative charge of the noncopper cations should be employed, e.g., Y(Ca)Ba(La)CuO.[4]

One may question the validity of our approach, as well as that of other approaches,[2,8] to the analysis of $dT_c/dP$ in underdoped orthorhombic YBCO and related materials under conditions where the oxygen content is changed. In underdoped materials it is well known from the work of Benischke *et al.*[18] and Fietz *et al.*,[15] that strong pressure-induced oxygen vacancy ordering effects occur as the oxygen content is reduced below 7. This ordering is accompanied by very large values of $dT_c/dP$ at certain compositions. Such effects were not included in previous models. These effects seem to suggest that a third parameter may be required to describe the ''equation of state'' at these compositions. In the model presented in this work such reordering effects are already (or may in principle be) included through variation of $y_{\text{M-I}}$. For instance, besides its dependence on composition $x$, we suspect that $y_{\text{M-I}}$ would depend also on some oxygen-order parameter. (Such an assumption would be consistent with self-doping effects which take place without change in oxygen content.) However, as long as the explicit dependence of $y_{\text{M-I}}$ on oxygen order is not known, our analysis cannot be carried out.

One more point about the analysis: Almasan *et al.*[8] use instead of Eq. (3) an equation that can be written in the form $T_c=T_c^{\max}-A(\Delta n_h)^2$. Their expression for $dT_c/dP$, ignoring for moment the difference between $\Delta q$ and $\Delta n_h$, does not contain the $T_c/T_c^{\max}$ factor that appears in Eq. (4), since they assumed that $A$ is independent of pressure.[8] NZ make the same assumption regarding the parameter $A$.[4] This is not merely a semantic difference. As $A=CT_c^{\max}$, it is not possible to have *both* $C$ and $A$ independent of pressure at the same time, since $T_c^{\max}$ does depend on $P$. Analysis of our data according to the procedure of Almasan *et al.* and of NZ, i.e., plotting $dT_c/dP$ against $\Delta q$ which is a modification of Eq. (5) assuming that $A$ (rather than $C$) is constant (not shown), yields a poor fit to a straight line.

The price of using our simple analysis is perhaps lack of microscopic insight on the charge-transfer term in Eqs. (4) and (5), since $q$ represents a macroscopic chemical doping parameter which is insensitive to the hole redistribution within the unit cell. However, it should be borne in mind that any microscopic theory intended at explaining pressure effects on $T_c$ has to agree with our simple linear analysis.

It would be desirable to extend these studies to materials that obey the same ''equation of state'' [Eq. (3)] with $\Delta q$ defined either by the anion or cation charge, which can be prepared also in the overdoped regime. In this way the most reliable values of $d\Delta q/dP$ and, in particular, of the difficult to measure parameter $dT_c^{\max}/dP$ will be obtained.

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