

Pressure dependence of the superconducting transition temperature of $\text{YBa}_2\text{Cu}_3\text{O}_7$ as a function of carrier concentration: A test for a simple charge-transfer model

J. J. Neumeier and H. A. Zimmermann

Sektion Physik, Universität München, Schellingstrasse 4, W-8000 München 40, Federal Republic of Germany and Walther Meissner Institut für Tieftemperaturforschung, W-8046 Garching, Federal Republic of Germany

(Received 13 January 1993)

Measurements of the superconducting transition temperature T_c vs purely hydrostatic pressure ($P < 0.6$ GPa) on specimens of compositions $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq x \leq 0.14$) and $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq y \leq 0.06$) yield an approximately linear relation between dT_c/dP and the carrier concentration induced in the CuO_2 planes by chemical substitution with dT_c/dP ranging from -0.6 K/GPa ($y=0.06$) to $+2.2$ K/GPa ($x=0.14$). A simple phenomenological model clarifies the dT_c/dP behavior and provides a physical origin for the observed anomalous peak in $T_c(P)$ at $P \sim 4$ GPa [Klotz, Reith, and Schilling, *Physica C* **172**, 423 (1991)].

After almost six years of experimental and theoretical work,¹ a good qualitative understanding of the pressure dependence of the superconducting transition temperature T_c for the oldest high- T_c superconductor with $T_c > 90$ K $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$,² still lies beyond our grasp. A step forward has been made by scientists who have suggested that dT_c/dP may be strongly influenced by a pressure-induced alteration of the holelike carrier concentration.^{1,3} This proposal is supported by two experimental observations: (1) the hole concentration increases under pressure as ascertained by measurements of the Hall constant's pressure dependence^{1,4,5} and valence-bond-sum calculations⁶ and (2) T_c is strongly dependent on the hole concentration.^{7,8} An investigation⁹ of a $\text{YBa}_2\text{Cu}_3\text{O}_7$ -like system, $(\text{Yb}_{0.7}\text{Ca}_{0.3})(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{Cu}_3\text{O}_{7-\delta}$, showed that through variation of the oxygen concentration an approximately linear relation existed between hole concentration and dT_c/dP and that negative values of dT_c/dP could be obtained. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, reduction of oxygen content, and thereby reduction of the hole concentration, is known to increase dT_c/dP dramatically¹⁰⁻¹² although reduction of oxygen concentration increases the mobility of the remaining CuO chain site oxygen atoms and can lead to time-dependent T_c values.¹³ In principal, these oxygen reordering effects may be strongly influenced by pressure in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system as was observed in $\text{Tl}_2\text{Ba}_2\text{CuO}_z$ by Sieburger and Schilling.¹⁴ With the objective of limiting these effects we focus our study on only *fully oxygenated* specimens. We present a simple chemical-substitution experiment designed to highlight *and* isolate the influence of the change in the hole concentration under pressure $\partial n/\partial P$ on dT_c/dP . Our herein-presented phenomenological model (1) provides a physical understanding of the observed linearity between dT_c/dP and the carrier concentration *induced by chemical substitution*, (2) yields an estimate of $\partial n/\partial P$ showing clearly that it *reduces* dT_c/dP in undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and (3) describes $T_c(P)$ of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the range $0 < P < 20$ GPa yielding excellent agreement with experi-

ment^{15,16} and a physical origin for the observed anomalous peak at $P \sim 4$ GPa.

Specimens of composition $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq x \leq 0.14$) and $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < y \leq 0.06$) were prepared as already described¹⁷ except that Al_2O_3 crucibles were used for the $0 \leq y \leq 0.06$ specimens. Powder x-ray diffraction indicated that all specimens were single phase. Iodometric titration¹⁸ was utilized to determine the oxygen concentration ($7-\delta$) to an estimated accuracy of ± 0.01 under the assumption that Y(La), Ba(Ca), Cu, and O in the presence of excess I^- in acidic solution under Ar atmosphere have the valences of +3, +2, +1, and -2, respectively. Electrical resistivity at ambient pressure was measured with a standard four-contact dc technique whereby reversal of the current cancels out thermoelectric voltages; typical current densities were 300 mA/cm². Temperature was measured to an absolute accuracy of ± 0.05 K with a calibrated Pt thermometer which was thermally anchored next to the specimen on the Cu sample holder. The values of T_c under high pressure were determined by measurements of the electrical resistivity at a frequency of 18 Hz; typical current densities were 30 mA/cm². High pressures ($P < 0.6$ GPa) were generated with a He gas compressor and transmitted through a Cu-Be capillary to the pressure cell in a He flow cryostat. The pressure was constantly monitored during the experiment to an accuracy of ± 3 MPa with a calibrated Manganin resistor residing at the compressor side of the capillary which is at room temperature. As long as one remains at *any* temperature above the melting curve of ⁴He,¹⁹ which is always the case in the temperature and pressure ranges of this study, the pressure transmitting medium is *purely* hydrostatic and pressure may be varied with the compressor. Measurement of T_c at ambient pressure, before and after pressure was applied, yielded identical T_c values indicating that the pressure medium has no influence on superconducting properties.

Results of the iodometric titration measurements for the La containing specimens have been published else-

where;¹⁷ we simply state the result that the oxygen concentrations for $0 \leq x \leq 0.14$ are scattered with $7-\delta = 6.96 \pm 0.02$. The oxygen concentrations for the $y = 0.015, 0.03, \text{ and } 0.06$ specimens are 6.98, 6.97, and 6.97, respectively. The observation that no oxygen is systematically absorbed or liberated in order to compensate for the holes filled or created indicates that the Cu valency (and holelike carrier concentration in the CuO_2 planes) decreases and increases for La and Ca substitution, respectively. This point has already been discussed in detail.^{8,17} More precisely, if we approximate the change in the carrier concentration in the CuO_2 planes per formula unit induced by chemical substitution and pressure as

$$n(x, y, P) = n(x, y) + (\partial n / \partial P)P, \quad (1)$$

where $n(x, y)$ is the carrier concentration induced by chemical substitution,²⁰ at ambient pressure $\partial n / \partial x \approx -1$ and $\partial n / \partial y \approx 1$ for the ranges of x and y here considered. In Fig. 1 our results of T_c vs x and y are displayed. In this discussion we define the temperature T_z as the temperature at which the electrical resistivity reaches the fraction z of the extrapolated normal-state resistance ($T_c \equiv T_{0.5}$) and the transition width $\Delta T_c \equiv T_{0.9} - T_{0.1}$ (denoted by the error bars in the figure). One sees that T_c clearly passes through a maximum as a function of the

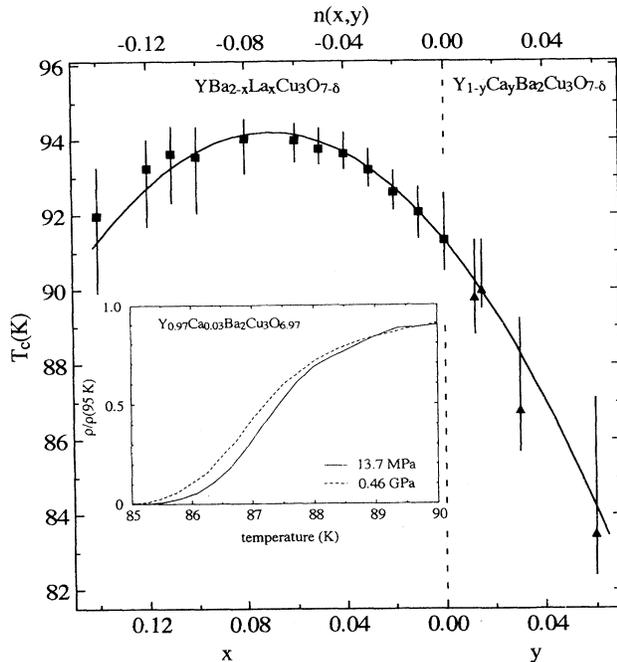


FIG. 1. Superconducting transition temperature T_c vs La (x) and Ca (y) concentrations (bottom axis) and hole concentration induced by chemical substitution $n(x, y)$ (top axis) at ambient pressure. T_z is defined as the temperature at which the electrical resistivity reaches the fraction z of the extrapolated normal-state resistance ($T_c \equiv T_{0.5}$) and the transition width $\Delta T_c \equiv T_{0.9} - T_{0.1}$ (denoted by the error bars in the figure). The solid line is a fit to the data. In the inset normalized electrical resistivity vs temperature is plotted for $\text{Y}_{0.97}\text{Ca}_{0.03}\text{Ba}_2\text{Cu}_3\text{O}_{6.97}$ at the indicated pressures.

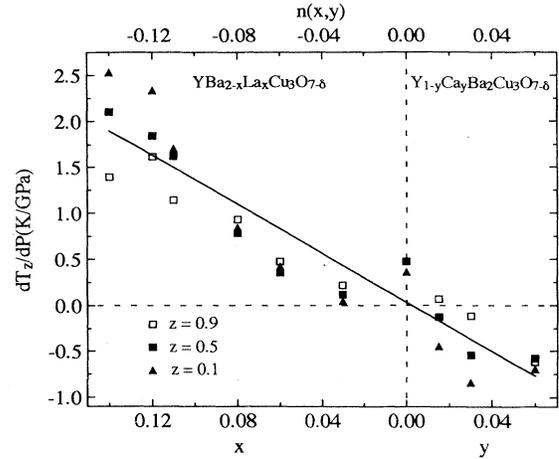


FIG. 2. dT_z/dP vs La (x) and Ca (y) concentrations (bottom axis) and hole concentration induced by chemical substitution $n(x, y)$ (top axis). T_z is defined as the temperature at which the electrical resistivity reaches the fraction z of the extrapolated normal-state resistance. The triangles, filled squares, and the open squares are determined from the $T_{0.1}(P)$, $T_{0.5}(P)$, and the $T_{0.9}(P)$ values, respectively. The solid line is a least-squares fit to the $dT_{0.5}/dP$ points.

hole concentration with T_c for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ residing on the $n(x, y) > 0$ side of the peak. This particular point was suggested by an independent investigation.⁸ A recent study¹⁷ illustrated that lattice compression due to the substitution of the smaller La^{3+} ion for Ba^{2+} cannot account for the increase of T_c . We note that an increase of T_c of ~ 2 K with a slight reduction of hole concentration has been observed with substitution of La^{3+} for Ba^{2+} (Refs. 17 and 21) as well as for a slight reduction of oxygen concentration $6.90 < 7-\delta < 6.97$ (Refs. 22 and 23) in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The solid line in Fig. 1 is a fit to the data at $P=0$ given by

$$T_c(n) = T_c^{\max} - A \left[\alpha + n(x, y) + \frac{\partial n}{\partial P} P \right]^2, \quad (2)$$

where $T_c^{\max} = 94.2$ K is the maximum T_c value, $A = 590$ K/hole² (all hole concentrations are stated per $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ formula unit), and $\alpha = 0.07$ holes.

Typical electrical resistivity curves under pressure for a $y = 0.03$ specimen are shown in the inset of Fig. 1 where it can be seen that pressure reduces T_c at this Ca concentration. This is the first observation of $dT_c/dP < 0$ in a fully oxygenated copper-oxide high- T_c superconductor with holelike charge carriers.¹ Our measurements of T_c under hydrostatic pressure for ten specimens are collectively displayed in Fig. 2. All $T_z(P)$ curves were linear in the range $0 < P < 0.6$ GPa. The data points represent the slope of the $T_{0.1}(P)$, $T_{0.5}(P)$, and the $T_{0.9}(P)$ curves and therefore all information concerning pressure-induced transition broadening is included in Fig. 2. Generally, pressure was altered at $T \sim 100$ K. In three of the dT_c/dP measurements ($x = 0.11$ and 0.14 and $y = 0.03$) we warmed the specimens to $T > 290$ K under pressure

followed by cooling and measurement of T_c . The $T_z(P)$ points obtained fell on the same curve as those where pressure was increased at 100 K. We therefore have no reason to believe that potential oxygen reordering effects¹⁴ are influencing dT_c/dP in these fully-oxygenated specimens. If we focus on the Ca side of the plot, we see that very small concentrations of Ca cause a depression of dT_c/dP and reversal of sign. On the La side, a decrease of the hole concentration causes a slight reduction of dT_c/dP followed by an increase. The scatter in the region $x=y=0$ could be attributable to small impurity concentrations of Al (in the $0 \leq y \leq 0.06$ specimens) or Ca (in the $0 < x \leq 0.14$ specimens) from the Al_2O_3 and Ca-stabilized ZrO reaction crucibles. A least-squares fit to the $dT_{0.5}/dP$ values reduces the influence of impurity effects on the following analysis and yield $dT_c/dP = 0.03 - 13.32n(x,y)$. We note that these results are in qualitative agreement with Miyatake *et al.*⁹ but that our study (1) comprises a range of $n(x,y)$ approximately half the size with more data points, (2) utilizes *undoped* $YBa_2Cu_3O_{7-\delta}$ as the reference specimen, and (3) utilizes fully oxygenated specimens.

The fact that T_c is dependent on the hole concentration coupled with the experimental observation⁴⁻⁶ that $\partial n/\partial P > 0$ suggests that $\partial n/\partial P$ will influence dT_c/dP . We can separate this effect from all others which influence dT_c/dP by postulating

$$\frac{dT_c}{dP} = \frac{dT_c^i}{dP} + \left[\frac{\partial T_c}{\partial n} \right] \left[\frac{\partial n}{\partial P} \right]. \quad (3)$$

The first term dT_c^i/dP represents the part of dT_c/dP not influenced by $\partial n/\partial P$ while the change in T_c with hole concentration is given by $\partial T_c/\partial n$. A similar equation has already been presented^{12,24} although significant differences exist. Kosuge *et al.*²⁴ did not include dT_c^i/dP in their considerations. The term in Almasan *et al.*¹² which would correspond to the first term on the right-hand side of Eq. (3), is for dT_c/dP at the peak in T_c vs $n(x,y)$. This is an important distinction which reflects that our objective is to establish dT_c^i/dP and $\partial n/\partial P$ for *undoped* $YBa_2Cu_3O_{7-\delta}$. Through calculation of $\partial T_c/\partial n$ from Eq. (2) and substitution into Eq. (3) we obtain

$$\frac{dT_c}{dP} = \frac{dT_c^i}{dP} - 2A \left[\alpha + n(x,y) + \frac{\partial n}{\partial P} P \right] \frac{\partial n}{\partial P}. \quad (4)$$

Immediately we see that dT_c/dP is linear in $n(x,y)$ (Ref. 20) as observed in Fig. 2. In addition, at $n(x=y,y=0)=0$, dT_c/dP in $YBa_2Cu_3O_{7-\delta}$ is reduced by the positive value of $2A\alpha\partial n/\partial P$. This is clear since, as shown in Fig. 1, T_c of $YBa_2Cu_3O_{7-\delta}$ lies on the $n(x,y) > 0$ side of the T_c vs $n(x,y)$ curve where an increase of $n(x,y)$ results in a reduction of T_c .

Comparing the slope of our fit in Fig. 2 with Eq. (4) allows us to estimate $\partial n/\partial P = +0.011$ holes/GPa. Taking the number of holes per formula unit in the CuO_2 planes²⁵ as 1.0, we obtain $(1/n)\partial n/\partial P \approx 1.1\%/GPa$. We note that this value is similar to $(1/n)\partial n/\partial P \approx 1.3\%/GPa$ obtained by bond-valence-sum calculations carried out on structure data.⁶ Hall effect

measurements under pressure^{1,4,5} yield $(1/n)\partial n/\partial P < 10\%/GPa$. Use of Eq. (4) and our intersect value of $dT_c^i/dP = 0.03$ K/GPa at $x=y=0$ allows us to estimate $dT_c^i/dP = 0.96$ K/GPa. This implies the $\partial n/\partial P$ term in Eq. (4) significantly reduces the observed value of dT_c/dP in undoped $YBa_2Cu_3O_{7-\delta}$. This is a crucial point which has not been considered in previous studies.^{9,12,24}

Now that we have established the parameters in Eq. (4), let us calculate $T_c(P)$ for undoped $YBa_2Cu_3O_{7-\delta}$. We integrate Eq. (4) utilizing $T_{0.5} = 91.30$ K thereby obtaining

$$T_c(P) = 91.30 \text{ K} + \frac{dT_c^i}{dP} P - A \left[2\alpha + 2n(x,y) + \frac{\partial n}{\partial P} P \right] \frac{\partial n}{\partial P} P. \quad (5)$$

We point out that the lattice compressibility¹ in the *entire* range $0 < P \leq 20$ GPa is a smooth well-behaved function (i.e., no phase transitions) and make the approximation that $n(0,0,P)$ remains linear to 20 GPa. Using our estimated value of $\partial n/\partial P = 0.011$ holes/GPa with $dT_c^i/dP = 0.96$ K/GPa we calculate the $T_c(P)$ curves shown in Fig. 3 in the range $0 < P < 20$ GPa for three values of $n(x,y)$. A decrease of $n(x,y)$ moves the $T_c(P)$ peak to higher pressures and strongly increases dT_c/dP at $P \sim 0$. We stress that *only* the parameters obtained from fits to the data in Figs. 1 and 2 and the herein-presented model are utilized for this calculation. For comparison, data from Klotz, Reith, and Schilling¹⁵ and Tissen and Nefedova¹⁶ are displayed. The general behavior of the data from both studies, including the anomalous peak in $T_c(P)$, is described remarkably well by this simple model when a value of $n(x,y)$ is chosen in the

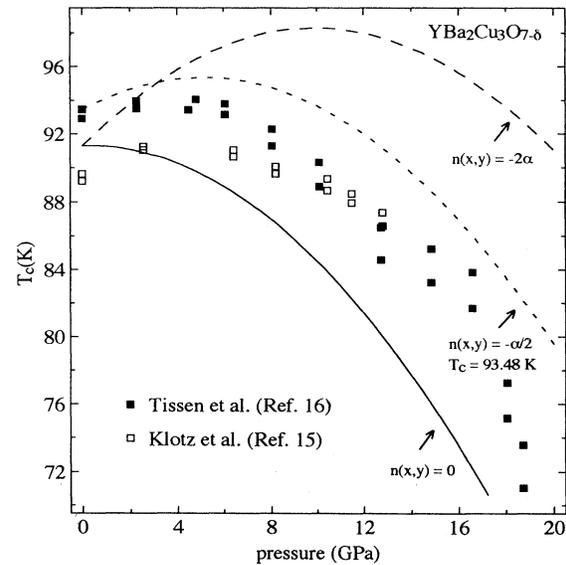


FIG. 3. T_c vs pressure for $YBa_2Cu_3O_{7-\delta}$. The data points are from measurements of the midpoint and onset of T_c by Klotz, Reith, and Schilling (Ref. 15) (open symbols) and Tissen and Nefedova (Ref. 16) (filled symbols). The lines are calculated with Eq. (5) for the indicated $n(x,y)$ values.

range $-\alpha/2 < n(x,y) < 0$ (corresponding to an increase in δ of $\Delta\delta \leq 0.0175$). The disagreement in $T_c(P=0)$ values of these two experiments, which causes the data of Klotz, Reith, and Schilling to lie somewhat below our curve, is unknown.

The inconsistencies in early measurements of $T_c(P)$ in the range $0 < P < 2$ GPa,^{1,26} especially the numerous values of dT_c/dP at $P=0$, can be qualitatively understood within the framework of the model presented herein. Any experimental factor which alters the carrier concentration in the CuO_2 planes thereby moves T_c on the parabolic curve and can succeed in changing the magnitude and/or sign of $\partial T_c/\partial n$ in Eq. (3). Tiny concentrations of impurities (less than a few atomic percent), possibly diffused into single crystals during the growth process or oxygen deficiency may accomplish this. The result could be dT_c/dP remaining positive to high pressures and even yielding T_c values higher than in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at comparable pressure as observed for $\delta=0.19$.¹¹ We show an example of this behavior in Fig. 3 where $T_c(P)$ was calculated using Eq. (5) with $n(x,y)=-2\alpha$ (i.e., $\Delta\delta=0.07$), which does not alter $T_c(P=0)$ but brings it to the $n(x,y) < 0$ side of the peak, and dramatically increases dT_c/dP at $P=0$.

We have shown clearly that fully oxygenated hole-

doped superconductors can have negative values of dT_c/dP . Our experiments indicate that dT_c/dP of $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$ is very sensitively dependent on the hole concentration in the CuO_2 planes and is certainly also similarly influenced by small amounts of impurities which are capable of altering the hole concentration. We have presented a simple phenomenological model which successfully describes the influence of the changing hole concentration on dT_c/dP and utilized the parameters from our study and this model to calculate $T_c(P)$ to higher pressures, thereby providing a physical understanding for the observed^{15,16} anomalous peak in $T_c(P)$. We encourage investigators to measure $n(0,0,P)$ to high pressures in order to test our assumption of linearity to $P < 20$ GPa. Most importantly, we have successfully revealed the influence of $\partial n/\partial P$ on dT_c/dP thereby isolating $dT_c^i/dP=0.96$ K/GPa, which reflects a more significant quantity for describing the influence of pressure on the superconducting state in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system.

The authors wish to thank J. S. Schilling for valuable discussions and encouragement and C. Allgeier, K. Andres, S. Klotz, M. Kund, and R. Sieburger for informative discussions.

¹See references in J. S. Schilling and S. Klotz, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsburg (World Scientific, Singapore, 1992), Vol. III, p. 59.

² $7-\delta$ implies $\delta \sim 0.03$ unless stated otherwise.

³E. N. Van Eenige *et al.*, *Physica C* **168**, 482 (1990).

⁴I. D. Parker and R. H. Friend, *J. Phys. C* **21**, L345 (1988).

⁵C. Murayama *et al.*, *Physica C* **185-189**, 1293 (1991).

⁶J. D. Jorgensen *et al.*, *Physica C* **171**, 93 (1990).

⁷M. W. Schafer, T. Penney, and B. L. Olson, *Phys. Rev. B* **36**, 4047 (1987).

⁸J. J. Neumeier *et al.*, *Phys. Rev. Lett.* **63**, 2516 (1989).

⁹T. Miyatake *et al.*, *Phys. Rev. B* **44**, 11 971 (1991).

¹⁰I. V. Medvedeva *et al.*, *Z. Phys. B* **81**, 311 (1990).

¹¹B. Bucher *et al.*, *J. Less-Common. Met.* **164-165**, 20 (1990).

¹²C. C. Almasan *et al.*, *Phys. Rev. Lett.* **69**, 680 (1992).

¹³B. W. Veal *et al.*, *Phys. Rev. B* **42**, 4770 (1990).

¹⁴R. Sieburger and J. S. Schilling, *Physica C* **173**, 403 (1991).

¹⁵S. Klotz, W. Reith, and J. S. Schilling, *Physica C* **172**, 423 (1991).

¹⁶V. G. Tissen and M. V. Nefedova, *Sverkhprovodimost' Fiz. Khim. Tekh.* **3**, 999 (1990).

¹⁷J. J. Neumeier, *Appl. Phys. Lett.* **61**, 1852 (1992).

¹⁸A. I. Nazzari *et al.*, *Physica C* **153-155**, 1367 (1988), and references therein.

¹⁹I. L. Spain and S. Segall, *Cryogenics* **11**, 26 (1971).

²⁰Equation (1) is an expansion of first order in P . We will see that $(\partial n/\partial P)P$ is small compared to the carrier concentration in the CuO_2 planes and we assume (1) $\partial n/\partial P$ remains constant for the values of x and y here considered and (2) $n(0,0,P)$ is linear in P . The first assumption is not in conflict with Ref. 12, where the calculated value of $\partial n/\partial P$ exhibits a peak in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for $\delta > 0.1$ since we are outside of that range with $x=0.14$ corresponding to $\delta < 0.1$.

²¹A. Manthiram, X. X. Tang, and J. B. Goodenough, *Phys. Rev. B* **37**, 3734 (1988).

²²J. W. Loram, J. R. Cooper, and K. A. Mirza, *Supercond. Sci. Technol.* **4**, S391 (1991).

²³H. Claus *et al.*, *Physica C* **198**, 42 (1992).

²⁴M. Kosuge *et al.*, *Phys. Rev. B* **45**, 10 713 (1992).

²⁵N. P. Ong, *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Vol. II, p. 459.

²⁶U. Koch *et al.*, *Solid State Commun.* **67**, 959 (1988).