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Pressure dependence of the superconducting critical temperature of the $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ system

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Using a cryogenic diamond anvil cell the pressure dependence of the superconducting transition temperature T_c of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ for $x=0.0, 0.1, 0.2,$ and 0.35 has been measured resistively up to ~ 20 GPa. In high- T_c superconductors there are two contributions to the pressure dependence of T_c : one related to pressure-induced charge transfer and one due to intrinsic effects. In the present experiment these contributions could be separated using a simple phenomenological model which incorporates the effect of changes in both the yttrium content x and the applied pressure p on T_c . In this system it is found that there hardly is any charge transfer by pressure so that the intrinsic pressure effect is the main contribution to $\partial T_c/\partial p$. The maximum T_c which can be reached in this system is 112 K. [S0163-1829(97)07517-6]

I. INTRODUCTION

Since the discovery of superconductivity in the Tl-Sr-Ca-Cu-O system^{1,2} it has taken some effort to improve the superconducting transition temperature T_c . The parent compound $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ (Tl-1212 phase) is a metal, showing no signs of superconductivity at all down to liquid helium temperatures. At room temperature (300 K) $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ has a resistivity of $7.2 \text{ m}\Omega \text{ cm}$ which gradually decreases as temperature is lowered. Extrapolation of the resistivity curve to 0 K gives a residual resistance of $2.8 \text{ m}\Omega \text{ cm}$. Moreover, the nominal copper valency in this compound is $+2.5$. All of this indicates an excess of holes on the CuO_2 layers giving rise to a so-called overdoped state. The number of holes on these layers can effectively be reduced by either substituting Pb^{4+} for Tl^{3+} or Y^{3+} for Ca^{2+} . As shown in Fig. 1, the structure of the resulting compound ideally is built up of alternating CuO_2 layers and (Tl,Pb)-O layers. The CuO_2 layers are essential for superconductivity to occur in these materials and are doped by the (Tl,Pb)-O layers which behave as charge reservoir as suggested by Hybertsen and Mattheiss³ on the basis of band structure calculations. By now it seems well established that the superconducting and normal state properties of these and other related ceramic compounds depend strongly on the charge carrier density n_h of the CuO_2 layers.^{4,5} The charge carrier density is defined as the number of holes per CuO_2 layer and copper atom.

A systematic investigation of $\text{Tl}_{1-y}\text{Pb}_y\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ was carried out by Liu *et al.*^{6,7} By optimizing the oxygen content for a number of compounds with different y and x , they were able to establish that at ambient pressure the highest T_c of ~ 110 K is found for $y=0.5$ and $x=0.2$. Since many related compounds show an increase of T_c with pressure^{5,8-11} it is tempting to also try to further increase the T_c of this system by applying pressure. Since the hole concentration is influenced both by

the lead content y and the yttrium content x , one of the two may be kept fixed and for the present study $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ was chosen.

This system with the Tl-1212 structure exhibits superconductivity over the entire range $0.0 \leq x < 0.6$. For $x=0.0$, T_c has a value of 78 K. With increasing yttrium content x , T_c increases to a maximum value of 108 K at $x=0.2$, and then decreases to 44 K at $x=0.5$. For $x \geq 0.6$, the system becomes semiconducting.

Apart from searching for the highest T_c , studying this

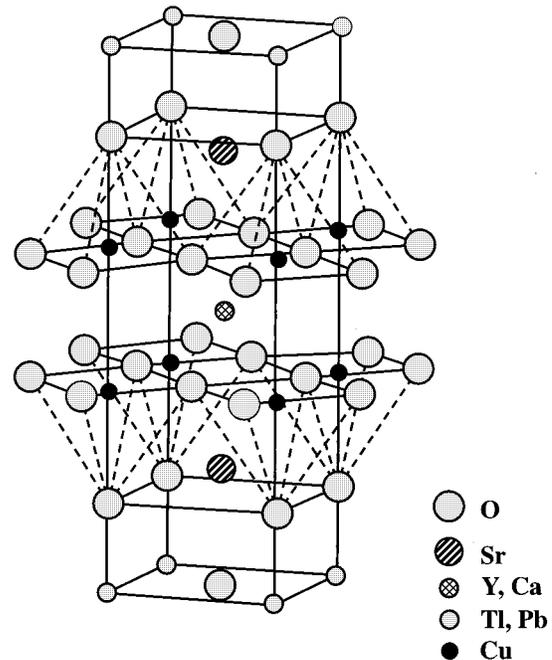


FIG. 1. Schematic representation of the crystal structure of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$. Ideally this structure is built up of alternating CuO_2 layers and (Tl,Pb)-O layers which act as charge reservoir (Ref. 3).

system may give important information on the pressure dependence of high- T_c superconductors. As is well known,^{12–19} the application of pressure not only changes the hole concentration on the CuO_2 layers, but also changes their maximum $T_{c\text{max}}$ as a function of hole concentration. By studying the pressure dependence of samples with different hole concentrations (i.e., different yttrium content x) these two effects can be discerned experimentally. This was done previously at *ambient pressure* by, for instance, Neumeier and Zimmermann¹⁴ and by García-Muñoz *et al.*¹⁹

In this paper, the pressure dependence of T_c of various $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ samples is studied up to ~ 20 GPa. In Sec. II a phenomenological model is presented, which describes $T_c(x, p)$ in a single simple formula. After a description of the sample preparation and the experimental details in Secs. III and IV, it will be shown in Sec. V that the experimentally observed behavior of T_c with pressure for the different samples can be used together with the model of Sec. II to find both the intrinsic pressure dependence of T_c and the amount of pressure-induced charge transfer.

II. PHENOMENOLOGICAL MODEL

It is generally accepted that the superconducting critical temperature T_c in high- T_c superconductors varies approximately as an inverted parabola with the hole concentration n_h .^{20–23} Below a certain minimum hole concentration the compounds are not superconducting and in this region they show nonmetallic behavior. As the hole concentration on the CuO_2 layers is increased, T_c increases reaching a maximum value $T_{c\text{max}}$ at an optimal hole concentration $n_{h\text{max}}$. For still higher values of the hole concentration, T_c starts to decrease and eventually goes to zero. In this region the compounds behave as normal metals. In most high- T_c cuprates it appears that optimal doping occurs at^{22,23} $n_h \approx 0.16$. Compounds with a lower hole concentration are said to be *underdoped* while compounds with a higher hole concentration are said to be *overdoped*. This behavior can be expressed^{24–26} by the following simple equation:

$$T_c(n_h) = T_{c\text{max}}[1 - \beta(n_h - n_{h\text{max}})^2]. \quad (1)$$

Considerable effort has been devoted in recent years to elucidate the pressure dependence of the superconducting transition temperature of high- T_c superconductors. High-pressure experiments on these compounds are done in the hope that they provide some answers as to why superconductivity occurs at such high temperatures. They may also provide important clues in order to synthesize other superconducting compounds with even higher T_c 's at *ambient pressure*.²⁷ The important information on the mechanism of superconductivity is contained in the pressure dependence of $T_{c\text{max}}$ [see Eq. (1)]. Unfortunately, due to the strong pressure dependence of n_h , the pressure dependence of $T_{c\text{max}}$ is generally very difficult to find. As will be shown below, the present study of a series of compounds with, at ambient pressure, different values of n_h , allows one to derive $T_{c\text{max}}(p)$. This is possible even if the pressure dependence of β and $n_{h\text{max}}$ is taken into account.

The pressure dependence of n_h is due to charge transfer from the (Tl,Pb)-O layers in $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ to the CuO_2 layers as a result of the contraction of the Cu-

(apical) O bondlength²⁸ which favors removal of antibonding electrons. Thus, pressure raises the hole concentration on the CuO_2 layers which explains the similarity between pressure and doping experiments. The following relation, therefore, is able to describe the T_c vs p behavior observed in many high- T_c compounds^{5,8,9}

$$T_c(p) = T_{c\text{max}}[1 - \alpha(p - p_{\text{max}})^2]. \quad (2)$$

In Sec. V it will be shown that even in $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$, where there is hardly any charge transfer by pressure, the experimental data can be reasonably described by this parabola.

III. SAMPLE PREPARATION AND CHARACTERIZATION

Samples with nominal composition $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ ($0 \leq x \leq 1$) were prepared by a solid state reaction as described in detail by Liu *et al.*^{6,7} and Liang *et al.*²⁹ High purity CaCO_3 , Y_2O_3 , SrCO_3 , and CuO powders from Aldrich Chemical Co. are thoroughly mixed in the appropriate stoichiometric amounts using a mortar and a pestle and subsequently calcined at 970°C for 12 h in air to form a precursor. This precursor is then mixed with Tl_2O_3 and PbO , ground, and finally pressed into a pellet (10 mm in diameter and 2 mm in thickness) under a pressure of 0.2 GPa. In order to prevent loss of thallium and lead during sintering in a furnace at 950°C for 3 h in flowing oxygen, the pellets are wrapped in gold foil. After sintering, the furnace is cooled down to room temperature at a rate of $5^\circ\text{C}/\text{min}$. As determined by powder x-ray diffraction measurements³⁰ all the members of the solid solution $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ ($0 \leq x \leq 1$) have the layered structure of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ (Tl-1212) belonging to the tetragonal $P4mmm$ space group (see Fig. 1). More importantly, these measurements confirmed that the sintered samples are homogeneous both in structure and composition.⁷

By now it has been established that substitution of Pb in the Tl sites,^{31–33} or Y in the Ca sites,^{34,35} not only stabilizes the crystal structure of the phase responsible for high temperature superconductivity but in addition also increases the volume fraction of superconducting material in the Tl-1212 phase. As mentioned in the Introduction and as previously proposed,⁶ substitution of Y^{3+} for Ca^{2+} in the system $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ effectively reduces the hole concentration on the CuO_2 layers. Several experimental findings seem to corroborate this. With increasing concentration of Y^{3+} in the Ca^{2+} sites, the following effects have been observed:^{6,7} (1) an increase in the a lattice parameter as determined from Rietveld refinement of neutron powder diffraction data, which generally is attributed to a decrease in the average copper oxidation state, leading to longer Cu-O distances within the CuO_2 layers, (2) an increase in the room temperature resistivity, (3) a decrease in the effective number of holes determined from Hall coefficient measurements, and (4) an increase in the absolute value of the thermoelectric power. Contrary to the increase in the a lattice parameter, the c lattice parameter decreases. This is probably due to the fact that in an eightfold coordination the radius of the Y^{3+} ion (1.019 Å) is slightly smaller than that of the Ca^{2+} ion (1.12 Å).³⁶

Several $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_7$ samples were subjected to annealing treatments⁷ which included slow cooling to 350 °C in oxygen and annealing at 500 °C and 600 °C in 2, 0.2, 0.009, and 0.0% of oxygen in nitrogen at 1 bar. Following each of these annealings no significant shift in the diamagnetic onset temperature of 108 K was observed. Liu *et al.*⁷ hence conclude that this compound with the highest T_c is very stable and does not exhibit any deviation of the oxygen stoichiometry. In all compositions the oxygen stoichiometry determined from neutron diffraction experiments was found to be very close to 7 and independent of the yttrium content x . As at ambient pressure, the sample with nominal composition $x=0.4$ showed a higher T_c value (extrapolated from the T_c vs p curve) compared to the one reported by Liu *et al.*⁷ it is not inconceivable that the small piece used in the high-pressure experiment had a slightly lower yttrium content with as result a higher hole concentration and hence a higher T_c value. Using T_c as a calibration, x should have a value of ~ 0.35 (see Ref. 7) instead of 0.4. Throughout the rest of this paper this value will be used in the calculations and the sample is consequently labeled $x=0.35$.

IV. EXPERIMENTAL DETAILS

Pressure is generated and applied to the samples using a cryogenic diamond anvil cell³⁷ (DAC). Its principle of operation is described in detail by Scholtz *et al.*³⁷ and by Tristan Jover *et al.*^{10,38} The applied pressure is determined *in situ*, close to the superconducting transition of the samples, with the ruby fluorescence method. After correction for the temperature-induced shift of the ruby R_1 fluorescence line,³⁹ the calibration of Mao *et al.*⁴⁰ is used. All experiments are made with the same pressure cell. The pressure is always changed at ~ 185 K and the data points are taken with increasing pressure only.

The temperature of the sample is measured using a standard platinum resistor placed in a copper block in which one of the diamonds is mounted. Since at low temperatures diamond has an even higher thermal conductivity than copper, there is good thermal contact between sample and thermometer. To check for possible thermal gradients in the body of the high-pressure cell, two other platinum resistors are mounted approximately 1 cm above and below the diamond anvils. The temperature difference is found to be 0.6 K. Interpolated linearly, this corresponds to a temperature difference across the sample of 3 mK.

The superconducting transition temperature T_c of the sample is determined resistively using the standard four-probe technique. The electrical leads are placed on top of one of the diamonds. These leads consist of flattened gold wires with a diameter of 25 μm which are pressed onto the sample for electrical contact. The four-point resistance $R(T)$ of the sample as a function of temperature is then measured with a Keithley 2001 multimeter using a current of 1 mA.

V. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 2 the T_c values at ambient pressure (extrapolated values from the T_c vs p curves) of the investigated samples are plotted as a function of the yttrium content x . While the

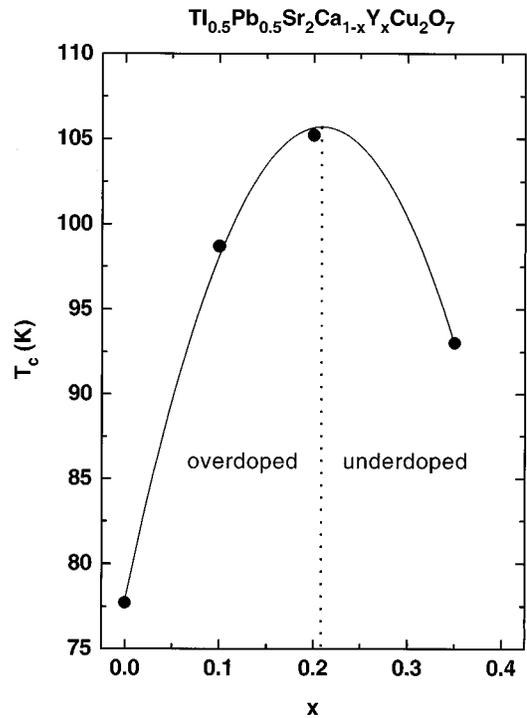


FIG. 2. The superconducting transition temperature T_c of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ vs yttrium content x at ambient pressure. For $x < 0.21$ the samples are overdoped while for $x > 0.21$ they are underdoped. Optimal doping is almost reached in the $x=0.2$ sample. The solid line is a parabolic fit (see text) to the experimental data.

$x=0.0$ and $x=0.1$ samples are overdoped, the $x=0.35$ sample is clearly underdoped. The $x=0.2$ sample is only slightly overdoped.

The T_c vs x behavior reflects the parabolic dependence of T_c vs n_h as described by Eq. (1), since the chemical doping x leads to a change in doping n_h ; in fact $n_h \propto -x$. Therefore the quadratic function $T_c(x) = a_0 + a_1 x + a_2 x^2$ was used to fit the experimental data in Fig. 2 (solid line). With T_c in units of K, the fitting parameters are $a_0 = 77.9$, $a_1 = 266.7$, and $a_2 = -639.3$. From this fit the optimum value of x at ambient pressure is found to be $x_{\text{max}} = 0.21$ with $T_{c\text{max}} = 105.7$ K, i.e., slightly lower than the maximum value reported previously.^{6,7}

Figure 3 shows typical superconducting transitions for the $x=0.2$ sample at two different pressures. The resistance curves are normalized with respect to their values measured at 80 K. As indicated on the 2.5 GPa curve in Fig. 3, the superconducting transition temperature T_c is defined as the intersection of the tangent through the inflection point of the resistive transition with a straight line fit of the normal state just above the transition. A clear shift of T_c towards higher values is observed in going from 2.5 GPa to 10.8 GPa.

Above T_c the resistance increases with decreasing temperature. This is attributed to the presence of intergrain boundaries in these samples, which have a measured density of the order of 55–65% of the theoretical density, and hence is not related to superconductivity at all. From scanning electron microscopy the grain sizes are found to be approximately 1 μm for all the compositions investigated in this

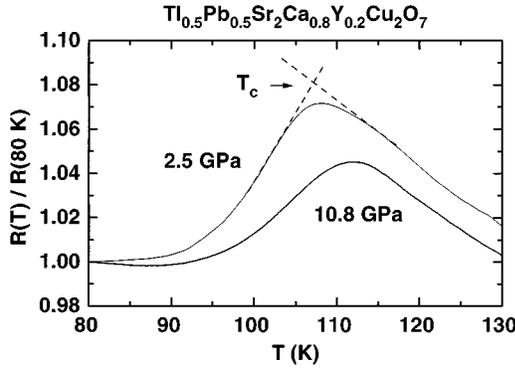


FIG. 3. Typical resistance curves of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_7$ at two different pressures. The curves are normalized with respect to the resistance values measured at $T=80$ K. The superconducting transition temperature T_c is defined as the intersection of the tangent through the inflection point of the resistive transition with a straight line fit of the normal state just above the transition as shown by the dashed lines. A clear shift of T_c towards higher values is observed in going from 2.5 GPa to 10.8 GPa.

work. This background fortunately has only a very limited effect upon the determination of T_c .

The T_c values obtained for all four samples are plotted as a function of pressure in Fig. 4. A parabolic pressure dependence of T_c is found for all samples except for the one with $x=0.0$. This sample shows an approximate linear T_c vs p dependence. For the nearly optimal doped sample ($x=0.2$) T_c reaches a maximum value of 112 K at ~ 8 GPa. A further increase in pressure only leads to a decrease in T_c . A similar behavior is also seen in the $x=0.1$ and $x=0.35$ samples.

In agreement with Eq. (2), the quadratic function

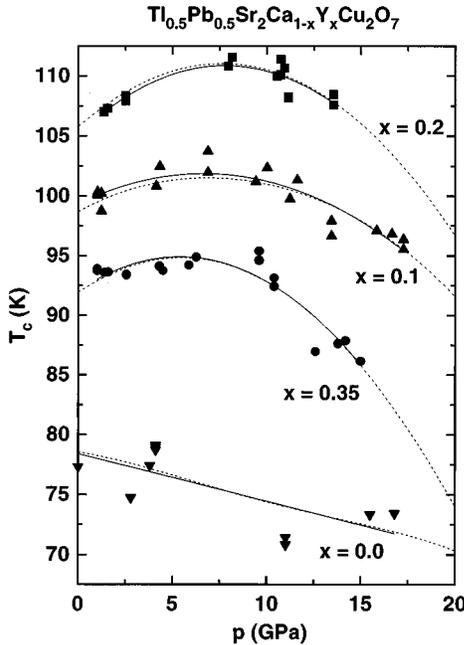


FIG. 4. Pressure dependence of T_c of four differently doped $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ samples. The solid lines are fits to the experimental data using a parabolic T_c vs p dependence, while the dashed lines result from a full $T_c(x,p)$ fit (see text).

$$T_c(p) = b_0 + b_1 p + b_2 p^2 \quad (3)$$

was used to fit the experimental data for each compound with different yttrium content x in Fig. 4 where T_c is expressed in K and p in GPa. The fit parameters b_i are given in Table I, the corresponding curves are the solid lines shown in Fig. 4. These fits will now be used to construct a single function $T_c(x,p)$ which describes all the data of Fig. 4. As a first step parabolas such as the one shown in Fig. 2, which holds for ambient pressure, are constructed at various pressures; i.e., the relation

$$T_c(x) = a_0 + a_1 x + a_2 x^2 \quad (4)$$

is constructed for $p=0, 2, \dots, 20$ GPa. Since in general the increment in pressure in the experiment is not constant, at each given pressure for all four x values the corresponding T_c values are obtained by the interpolation of Eq. (3) of which the appropriate coefficients are given in Table I.

As a result the fit parameters a_i are obtained at all pressure values considered. To obtain a single function $T_c(x,p)$, a smooth function can be fitted to the parameters $T_{c\text{max}}$, β^* , and x_{max} as a function of pressure after rewriting Eq. (4) as follows:

$$T_c(x,p) = \left(a_0 - \frac{a_1^2}{4a_2} \right) \left[1 - \left(\frac{-a_2}{a_0 - (a_1^2/4a_2)} \right) \left(x + \frac{a_1}{2a_2} \right)^2 \right] = T_{c\text{max}}(p) \{ 1 - \beta^*(p) [x - x_{\text{max}}(p)]^2 \}. \quad (5)$$

The pressure dependence of $T_{c\text{max}}$, β^* , and x_{max} is shown in Fig. 5. It turns out that in order to describe all these dependencies separately a simple quadratic function similar to Eq. (3) suffices. The fit parameters c_i so obtained for each function are given in Table II. Equation (5) together with these parameters now completely defines $T_c(x,p)$. As an example $T_c(x,p)$ may be calculated for $x=0.0, 0.1, 0.2$, and 0.35 . The result of this calculation is shown as the dashed lines in Fig. 4. Clearly $T_c(x,p)$ very closely fits the experimental data, which shows that the procedure used here is justified. Of course not only the fit to the experimental data can be calculated, but indeed the whole $T_c(x,p)$ landscape can be investigated. The result is shown as a contour plot in Fig. 6: the maximum T_c which can be reached in this particular system is 112 K. This value can be reached only under pressure at optimal yttrium content ($x=0.21$). As stated above, this analysis is done with a corrected concentration value of $x=0.35$ for one sample. If for this sample the nominal value $x=0.4$ (which applies for the bulk from which it was taken) is used, the quantitative analysis is slightly modified. For example, the maximum T_c would then occur for $x=0.23$,

TABLE I. By fitting the experimental data for each compound with different yttrium content x in Fig. 4 with the quadratic function Eq. (3), the following values for the fit parameters b_i are obtained.

x	b_0	b_1	b_2
0.0	78.4	-0.40	0
0.1	99.3	0.77	-0.057
0.2	105.2	1.5	-0.094
0.35	92.0	1.1	-0.098

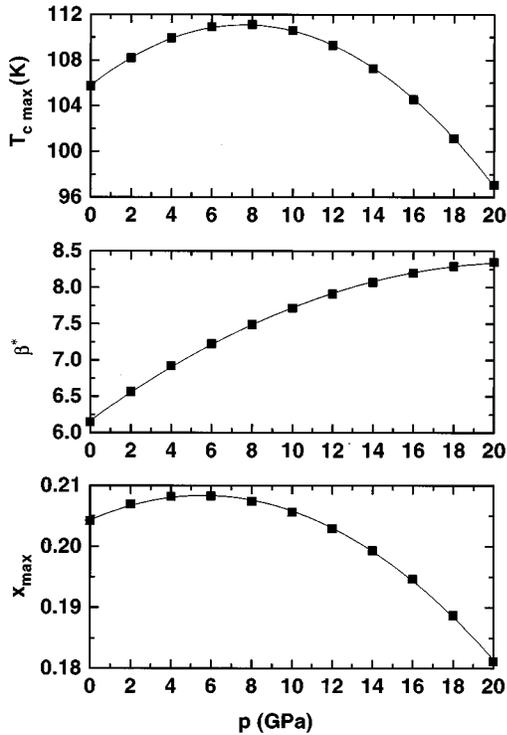


FIG. 5. The values of $T_{c,max}$, β^* , and x_{max} at $p=0,2,\dots,20$ GPa. The solid lines show the parabolic fits of which the parameters are given in Table II.

while the sharp dropoff at the upper right corner in Fig. 6 is reduced: the position of the 75 K isotherm as shown would then represent a 90 K isotherm.

Now Fig. 5 will be discussed in more detail. The pressure dependence of $T_{c,max}$, which represents the intrinsic pressure dependence of T_c , shows a maximum around 8 GPa, consistent with Fig. 4. In general, a maximum for $T_{c,max}$ as a function of pressure would be expected: due to the stronger coupling between CuO_2 layers T_c increases until the layers are too close and deformation or other detrimental effects take over. The parameter β^* defines the width of the parabola shown in Fig. 2, and corresponding ones at higher pressures. The increase of β^* with pressure implies a slight narrowing of the parabola, which means that T_c is more sensitively dependent upon doping, but also that the compound is superconducting in a narrower range of doping. In principle the parameter x_{max} contains two contributions due to (i) the effect of doping by Y^{3+} , Pb^{4+} and oxygen deficiency and (ii) the fact that the ambient pressure maximum of T_c vs n_h is not at $n_h=0$ but at $n_h=n_{h,max}\approx 0.16$. Incidentally, as

TABLE II. By fitting each of the parameters $T_{c,max}$, β^* , and x_{max} of Eq. (5) as function of pressure with a quadratic function $f(p)=c_0+c_1p+c_2p^2$, the following values for the fit parameters c_i are obtained.

	c_0	c_1	c_2
$T_{c,max}$	105.8	1.4	-0.092
β^*	6.2	0.21	-0.0049
x_{max}	0.20	0.0014	-0.00012

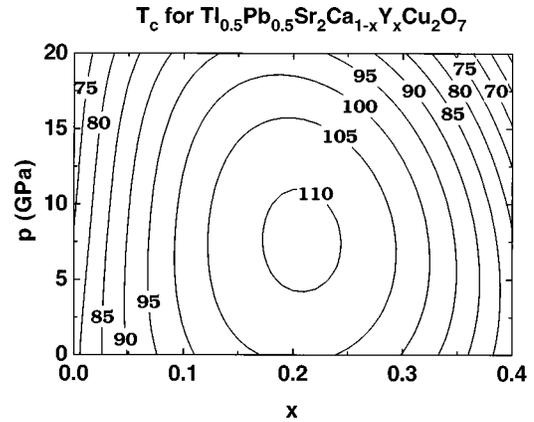


FIG. 6. Contour plot of $T_c(x,p)$. The maximum T_c which can be reached in this particular system is 112 K. This value can be reached only under pressure and at optimal yttrium content ($x=0.21$).

explained above there is practically no oxygen deficiency in these compounds and doping due to it can be ignored. The pressure dependence of x_{max} also contains these two contributions: the pressure-induced shift in $n_{h,max}$ and in doping by Y^{3+} and Pb^{4+} . Regrettably these two contributions cannot be separated in the present experiment.

It is of course interesting to try and relate x to n_h ; first the zero-pressure case is considered. As the high- T_c superconductors are usually considered to be *ionic*,⁴¹ charges can be assigned to each of the constituent cations (metal ions) and anions (oxygen ions) which are represented as point charges. Assigning the nominal valencies to the *ionic* constituents of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$, i.e., Tl^{3+} , Pb^{4+} , Sr^{2+} , Ca^{2+} , Y^{3+} , Cu^{2+} , and O^{2-} , the number of holes per CuO_2 layer per copper atom would be given by

$$n_h = 0.25 - \frac{x}{2}. \quad (6)$$

The validity of this relation can be easily checked. The parabola given by Eq. (1) yields precisely $T_c=0$ for $n_h = n_{h,max} \pm \sqrt{1/\beta}$. The width of the parabola at its base is thus given by $\Delta n_h = 2\sqrt{1/\beta}$; it is well known²⁰ that $\Delta n_h \approx 0.22$. Using the fit to the experimental data in Fig. 2 it is found that $\Delta x = 0.8$, where Δx is defined analogously to Δn_h . As a first approximation $n_h = \text{const} + (\Delta n_h/\Delta x)x$ or after substituting the values for Δn_h and Δx given above:

$$n_h = \text{const} - \frac{x}{3.6}. \quad (7)$$

Comparing this relation to Eq. (6), it becomes clear that the CuO_2 layers in this particular system benefit only from about half of the chemical doping. Possibly some charge is trapped elsewhere, or not all Y^{3+} replaces Ca^{2+} .

Now the magnitude of $\partial n_h/\partial p$ close to zero pressure is discussed. If the initial slope $\partial x_{max}/\partial p$ is entirely attributed to a change in the hole concentration n_h (to obtain an upper bound) then it is found that $\partial n_h/\partial p \approx 3.9 \times 10^{-4} \text{ GPa}^{-1}$, close to the value of $5 \times 10^{-4} \text{ GPa}^{-1}$ found⁴²⁻⁴⁶ for $\text{CaLaBaCu}_3\text{O}_7$. Both $\text{CaLaBaCu}_3\text{O}_7$ and

$\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ have a special crystal structure. In $\text{CaLaBaCu}_3\text{O}_7$ the doping of the CuO_2 layers is provided by the CuO chains, which are very short due to the formation of very small crystallites which make $\text{CaLaBaCu}_3\text{O}_7$ macroscopically tetragonal.⁴² Gupta and Gupta⁴⁷ have calculated that this severely hinders the transfer of charge and hence $\partial n_h / \partial p$ is expected to have a small value. In $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ the doping is provided by the (Tl,Pb)-O layers, which are also known to be of irregular nature. Due to this, charge transfer from the (Tl,Pb)-O layers to the CuO_2 layers is frustrated. Hence it is considered likely that in $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ pressure-induced doping of the CuO_2 layers is very small, although it cannot be ruled out that the change in doping from the (Tl,Pb)-O layers and the pressure-induced shift in $n_{h\text{max}}$ accidentally cancel. A small value for $\partial n_h / \partial p$ implies that pressure-induced charge transfer would have a small effect on T_c . Hence the extrinsic value of $\partial T_c / \partial p$ is small in this particular system.

VI. CONCLUSION

Using a cryogenic diamond anvil cell the pressure dependence of the superconducting critical temperature of several $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ samples has been measured resistively under quasihydrostatic conditions. The T_c vs p behavior for the different samples investigated can be explained in terms of a phenomenological model which basically involves two terms: one directly related to pressure-induced charge transfer and another more dominant one related to intrinsic effects.

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