



Intrinsic and carrier density effects on the pressure dependence of T_c of high-temperature superconductors

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Abstract

The pressure dependence of T_c in high-temperature superconductors is experimentally found to be influenced not only by a pressure-induced increase in charge carrier density but also by intrinsic effects. The influence of both contributions was systematically investigated in $Tl_{0.5}Pb_{0.5}Sr_2Ca_{1-x}Y_xCu_2O_7$. The behavior of superconductors with three or four CuO_2 -layers is further complicated by the inequivalence of the inner and outer CuO_2 -layers. High-pressure experiments up to 46 GPa are analyzed in view of the above. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Immediately after the discovery of high- T_c superconductivity high-pressure experiments have played an important role in improving and understanding these materials. Several review papers summarize these experiments [1–5]. Despite tremendous experimental (and theoretical) efforts, not only in the field of high pressure but extending to nearly all techniques known in solid state physics, the microscopic mechanism for high- T_c superconductivity is not yet clear, although progress is still made. Therefore, this discussion will necessarily be restricted to a consistent phenomenological description of the behavior of these interesting materials under pressure.

The rich variety in the behavior of T_c under pressure shown in Fig. 1 is essentially due to four ingredients. First, it is well known [6] from chemical-doping experiments that the critical temperature T_c of high- T_c superconductors is a function of the doping of the CuO_2 layers, which are responsible for the superconductivity in these materials. The function $T_c(n_h)$ is similar to an inverted parabola with a maximum for $n_h \simeq 0.2$, where n_h is the number of holes per Cu-atom of the CuO_2 layers. Secondly, it is known both from experiments [7–10,45–48] and calculations [11–13,49–53] that n_h increases with pressure. Hence $T_c(p)$ is expected to follow the $T_c(n_h)$ curve. Such approximate parabolic $T_c(p)$ curves are indeed observed for a number of compounds, see for example the curves for $YBa_2Cu_4O_8$ (◆) and $Y_2Ba_4Cu_7O_{15}$ below 20 GPa (+) in Fig. 1. Note that $T_c(p)$ does not need to be strictly parabolic due to the possible non-linear relation $n_h(p)$. Thirdly, in some high- T_c

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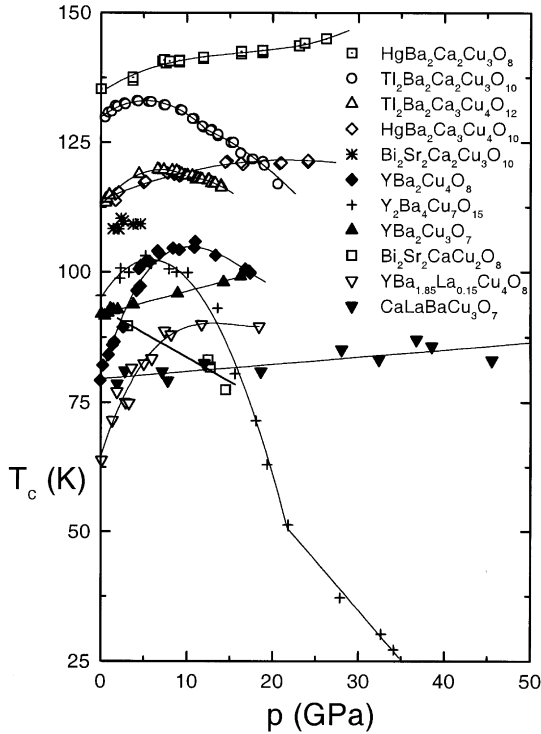


Fig. 1. $T_c(p)$ for the compounds indicated as measured in our laboratory.

superconductors inequivalent superconducting layers are present due to the peculiarities of the crystallographic structure. In one unit cell there are n adjacent CuO_2 layers between a top and bottom “block layer”, as illustrated schematically in Fig. 2. If $n \leq 2$, then all CuO_2 layers are equivalent, but for $n = 3$ and 4 there are two different kinds (inner and outer, shown white and grey, respectively) due to the different topology of their surroundings. The presence of the inequivalent layers may lead to more complicated $T_c(p)$ curves, for example consisting of parts of two parabolas. Fourthly, it is often found that the maximum T_c under pressure is higher than the maximum T_c at zero pressure (as a function of chemical doping), implying that there exists an intrinsic enhancement of T_c due to pressure.

After a brief description of our experimental technique, the influence of both doping and intrinsic effects on T_c under pressure is discussed

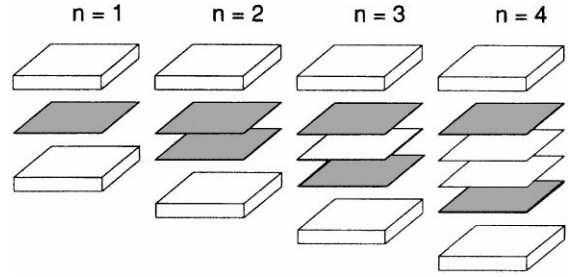


Fig. 2. Schematic representation of the crystal structure of the high- T_c superconductors. One unit cell consists of “block layers” (thick and white) and CuO_2 layers. If the number n of CuO_2 layers is three or four, there are topologically inequivalent inner (thin and white) and outer (thin and grey) CuO_2 layers.

for compounds with equivalent layers. Then the effects on $T_c(p)$ of inequivalent layers are discussed. The paper is concluded with some general observations.

2. Experimental technique

Experiments in our group are done in cryogenic diamond anvil cells (DACs) [14–16]. Pressure is determined from the ruby R_1 fluorescence [17] and temperature is measured from a calibrated platinum resistor thermally anchored to one of the diamonds. The superconducting T_c is measured by four-point resistometry either directly using a sensitive multimeter or (for low resistance samples) with a 0.5 Hz AC technique thus avoiding the effect of thermovoltages. We use the onset values for T_c , defined as the intercept between the tangents in the midpoint of the resistive transition and in the linear regime above T_c .

In view of the extreme pressures used, the tiny pieces of sample and the resulting not fully hydrostatic stress conditions, one may rightly ask whether results of such experiments are reliable. To address this question, in Fig. 3 experimental results of a number of different groups on $T_c(p)$ for $\text{YBa}_2\text{Cu}_4\text{O}_8$ are shown. This compound is chosen, because its doping is always the same, thus reducing the influence of different samples. Despite the different experimental techniques and pressure media, very nice agreement is obtained.

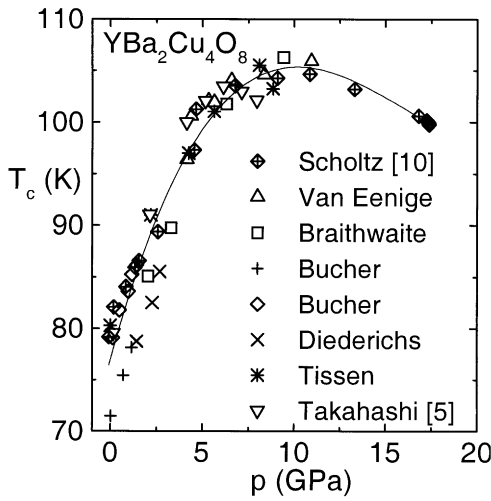


Fig. 3. Critical temperature T_c for $\text{YBa}_2\text{Cu}_4\text{O}_8$, which has a fixed oxygen stoichiometry. The line is a guide to the eye. The data shown is from different groups, using both single crystals and ceramic samples and different pressure transmitting media. Unless already indicated, references may be found in (Fig. 16 of) Ref. [4]. Clearly, there is good agreement between the various results.

This comparison shows that such experiments do yield reliable results, and that differences between experiments should be attributed to different properties of the samples used.

3. Intrinsic and doping effects on $T_c(p)$

To separate the intrinsic and doping effects on $T_c(p)$ mentioned in the introduction, the system $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ is investigated [18]. In this system there is only one kind of CuO_2 layer, making the results easier to interpret. The doping n_h of the CuO_2 layers can be simply changed by adjusting x , which is done by preparing various samples [19–21]. Thus samples are available which are at ambient pressure at different points on the $T_c(n_h)$ curve and in each of these T_c can be studied under pressure. The experimental results are summarized in Fig. 4, which is based on experimental data [18] for $x = 0.0, 0.1, 0.2$ and 0.35 . The full pressure and doping dependence shown can be expressed as $T_c(x, p) = T_c^{\text{max}}(p)[1 - \beta(p)(x - x_{\text{max}}(p))^2]$

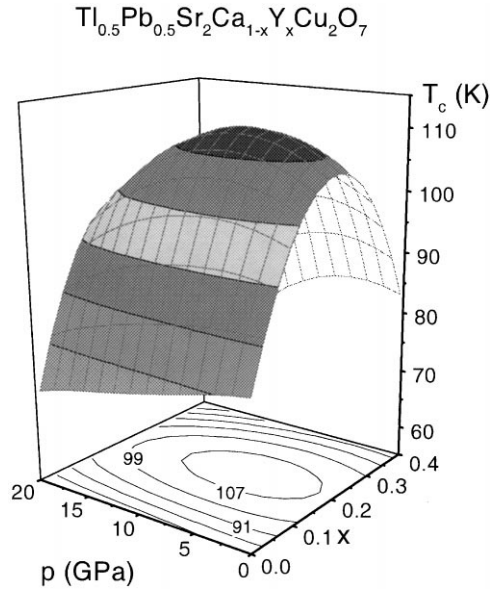


Fig. 4. T_c of $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$. At fixed pressure p , increasing x implies decreasing (hole) doping. However, due to pressure-induced doping, lines of constant x are not lines of constant doping.

where $T_c^{\text{max}}(p)$ describes the intrinsic pressure dependence of T_c , while $\beta(p)$ gives the width of the parabola $T_c(x)$ and $x_{\text{max}}(p)$ is the doping corresponding to the highest T_c at pressure p . These parameters are plotted in Fig. 5.

From Fig. 4 it is clear that pressure can increase T_c to a value higher than obtainable at any doping under ambient pressure. Note the clear optimum $T_c(7.6 \text{ GPa}, x = 0.204) = 111.1 \text{ K}$.

This proves the intrinsic effect of pressure on T_c in these materials: the increase in T_c cannot be due to more optimal doping, since the whole doping range is monitored under pressure. In fact, such intrinsic effect was already identified as early as 1990 in our group by Van Eenige et al. [22] after the observation that under pressure the T_c of optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ exceeded its zero pressure value (in this paper both the effect of doping and intrinsic effects are taken into account; it precedes the more detailed work on intrinsic effects by Neumeier and Zimmerman [23]). The intrinsic effect was also identified by us at an early stage in other compounds [24,25].

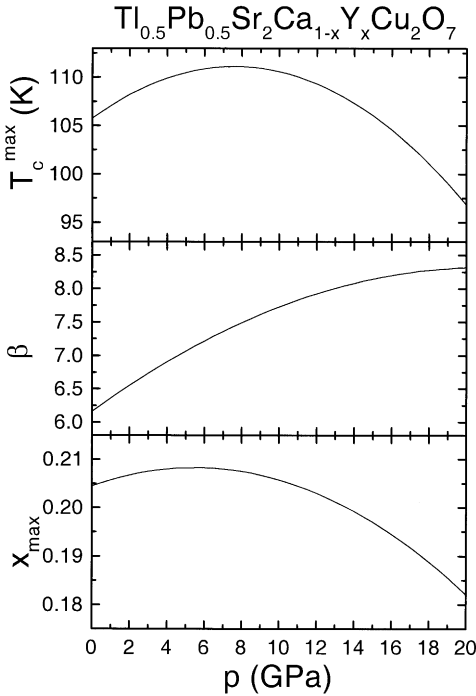


Fig. 5. The parameters $T_c^{\max}(p)$, $\beta(p)$ and $x_{\max}(p)$ for $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$. The intrinsic pressure dependence of T_c is due to the pressure dependence of T_c^{\max} .

Some general conclusions about the T_c of high- T_c superconductors with two CuO_2 layers (i.e. $n = 2$) can be made. The maximum value of 111.1 K for $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ can be compared to the highest values reported for other $n = 2$ compounds. The maximum (as a function of doping and pressure) reported is 108 K, except for Tl-based materials where the maximum [26] is 119 K and Hg-based compounds where values around 150 K have been reported [27,28]. Except for this last experiment there appears to be a maximum $T_c \approx 110$ –120 K for the $n = 2$ compounds. In Fig. 5 we also plot $\beta(p)$ which defines the width of the doping range where superconductivity occurs. The pressure-induced increase in β implies that this range narrows under pressure; a similar observation for $\text{HgBa}_2\text{CuO}_{4+\delta}$, but even more pronounced, was made by Qiu et al. [29]. From the behavior of x_{\max} in Fig. 5 it is clear 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

charge transfer does not play a dominant role. Again, a similar effect was noted [29] for $\text{HgBa}_2\text{CuO}_{4+\delta}$. It should be stressed, however, that in many other high- T_c superconductors charge transfer dominates $T_c(p)$. For example such charge transfer is found from calculations of the Madlung energies [11], Bond Valence Sums [12] and electronic structure [13,49–53], and in experiments such as neutron scattering [7], NQR [8,45,46], thermo-electric power, Hall-effect [9,47,48] and H_{c2} measurements [10]. In particular the correlation between $T_c(n_h)$ and $T_c(p)$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is very striking as shown previously [22,30]: e.g. high values for $\partial T_c/\partial p$ correlate very nicely with high values for $\partial T_c/\partial n_h$.

4. Compounds with inequivalent CuO_2 layers

In compounds with three or four CuO_2 layers ($n = 3$ or $n = 4$) one can discern “inner” and “outer” CuO_2 layers, see Fig. 2. The inner layers are sandwiched between other CuO_2 layers, while the outer layers are adjacent to one CuO_2 layer and one block layer. As a consequence of this inequivalence, the doping from the block layers may spread unevenly between the inner and outer CuO_2 layers. The charge distribution may be calculated from the model of Haines and Tallon [31]. In this model, the distribution of the charge carriers between the CuO_2 layers is found by minimizing the total energy $U_{\text{tot}} = U_{\text{band}} + U_{\text{Mad}}$ of the charge carriers. The kinetic energy is given by

$$U_{\text{band}} = \frac{\pi \hbar^2}{2m^* a^2} n_{\text{h}}^2,$$

where a is the (2D) lattice parameter and the effective mass is m^* . The total doping induced by the block layers is δ . Of this charge, a fraction $\frac{1}{2}(1-x)$ is transferred to each of the outer CuO_2 layers, while for $n = 3$ a fraction x resides on the (single) middle CuO_2 layer and for $n = 4$ a fraction $\frac{1}{2}x$ is transferred to each (of the two) middle CuO_2 layers. From these definitions it may easily be verified that

$$U_{\text{band}}(x) = \frac{\pi \hbar^2}{2m^* a^2} \delta^2 \left(\zeta x^2 - x + \frac{1}{2} \right)$$

with $\zeta = \frac{3}{2}$ for $n = 3$ and $\zeta = 1$ for $n = 4$. The Madlung energy is given by

$$U_{\text{Mad}} = \frac{e^2 \delta}{2\epsilon S} [b_0 + b_1 \delta + (b_2 + b_3 \delta)x + b_4 \delta x^2],$$

where ϵ is the effective dielectric constant which takes into account all charge carriers not in the bands under consideration, S is the average Wigner–Seitz radius and the b_i are coefficients [32] depending on the crystal structure and the *distribution* of the carriers between the copper and oxygen sites in the CuO_2 layers. By minimizing the total energy $U_{\text{tot}} = U_{\text{band}} + U_{\text{Mad}}$, and using the notation

$$A = \frac{e^2 a^2 m^*}{\hbar^2 \pi S \epsilon}$$

the distribution of holes between the layers is given by

$$x = \frac{1 - A(b_2/\delta + b_3)}{2(\zeta + Ab_4)}.$$

Thus a rather complicated behavior of $x(\delta)$ and hence of charge distribution as a function of pressure is in principle possible [33], but the most relevant possibility is an increase of doping n_h versus δ in both the inner and outer layers such that n_h of the outer layers is larger and increases at a faster rate with δ than the n_h of the inner layers (for a schematic picture see Fig. 8 of Ref. [34]). If the T_c of the sample as a whole is the maximum of the T_c 's of the layers, then $T_c(p)$ is first a parabola due to the outer layers and at higher pressures again a parabola due to the inner layers. In fact such behavior is beautifully displayed by the $n = 3$ and 4 thallium-based superconductors as demonstrated in Fig. 6 as a function of pressure, T_c first follows one parabola but above 12 (for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$) or 10 GPa (for $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$) T_c follows another parabola.

Another example of a compound with inequivalent superconducting units is the $n = 2$ compound $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$. This perovskite is in fact a naturally formed multilayer of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductors and the $T_c(p)$ behavior of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ can be predicted directly from the $T_c(p)$ behavior of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$, as was elegantly demonstrated by

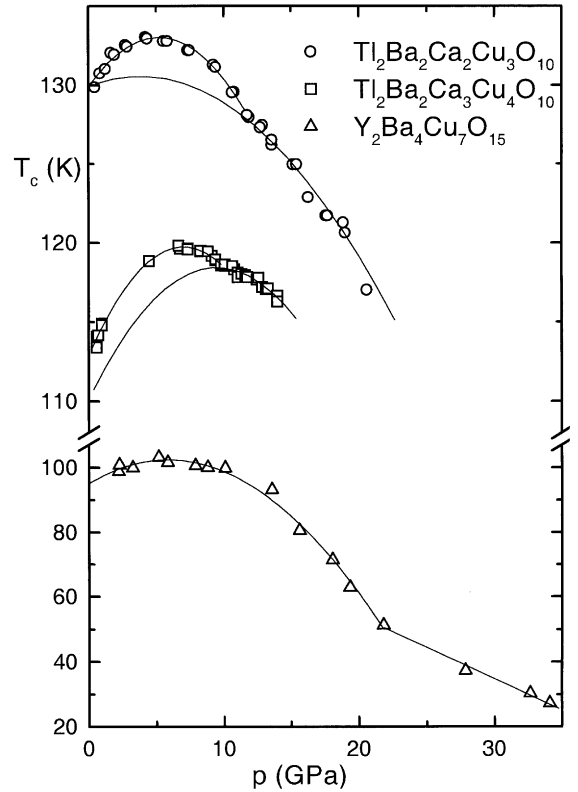


Fig. 6. $T_c(p)$ for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$ and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (from Refs. [33,35]). Note that $T_c(p)$ is not a simple parabola, but consists of two parabolae corresponding to $T_c(p)$ of the two inequivalent layers.

Van Eenige et al. [35]. Note also that the pressure-induced change in T_c for $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ is about 75 K (see Fig. 6), which is the largest pressure-induced change in T_c reported so far.

5. Discussion

We make first some general observations on high- T_c superconductors and discuss some general trends in their behavior under pressure. Then an attempt is made to use these ingredients for an explanation of our results as presented in Fig. 1.

As indicated above, the hole doping of the CuO_2 layers is increased by pressure. The rate may depend on compound and oxygen stoichiometry;

data for many compounds can be found in Ref. [30]. The maximum rate is approximately $\partial n_n / \partial p = 0.02 \text{ GPa}^{-1}$.

In a homologous series (e.g. the Hg-based superconductors) the same block layers provide the doping for a different number n of CuO_2 layers. Hence, for increasing n , the (average) doping will range from overdoped to underdoped [36]. In particular, the $n = 3$ compounds are slightly underdoped and the application of pressure will raise T_c by making the doping more optimal. Since T_c also increases due to intrinsic effects, both contributions cooperate in the $n = 3$ compounds, resulting in the occurrence of the highest T_c -values for any superconductor under pressure.

In view of the absence of a definite microscopic model for high- T_c superconductivity it is not possible to ascertain what the microscopic cause is for the *intrinsic* pressure effect. An interesting phenomenological model was put forward recently by Acha et al. [37]; like our treatment [35] for the $T_c(p)$ of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ it is based on the proximity effect. In this model the superconductor is a multilayer of superconducting and non-superconducting layers (see Fig. 2). The T_c of such a multilayer is in the Cooper–de Gennes model for proximity coupling given by $T_c = \theta e^{-1/\lambda}$ with $\lambda = (d_s N_s \lambda_s) / (d_s N_s + d_n N_n)$, where λ_s determines the intrinsic T_c of the superconducting layer by $T_c^s = \theta e^{-1/\lambda_s}$ and $d_s(d_n)$ is the thickness of the superconducting (normal) layer while the N_i are the densities of states. The parameter θ is a typical coupling energy for the Cooper pairs. With $\alpha = N_n / (\lambda_s N_s)$ we find from the above

$$\ln\left(\frac{T_{c1}}{T_{c2}}\right) = -\alpha\left(\frac{d_{n1}}{d_{s1}} - \frac{d_{n2}}{d_{s2}}\right). \quad (1)$$

Note that for certain superconductors, the d_{ij} are known from neutron scattering, even under pressure. Hence the only unknown is α . Acha et al. argue that $T_c(p)$ can be explained by the inhomogeneous compression of the different layers under external pressure. Due to this the thickness ratio of superconducting layers versus non-superconducting layers increases leading to higher T_c under pressure. To verify this idea we compare the T_c values for $\text{HgBa}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m+2}$ for vari-

ous m (where d_s increases with m) at ambient pressure with the T_c for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ under high pressure. Using Eq. (1) we find from the parameters of $\text{HgBa}_2\text{CuO}_4$, $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ that $\alpha = 0.12 \pm 0.03$. By contrast Acha et al. find $\alpha = 1.00 \pm 0.02$ (note that their $[N(0)V]_s$ is our α). Clearly, these results are inconsistent: the pressure dependence of T_c cannot be explained only on the basis of a pressure-induced enhancement of proximity coupling.

In contrast to the model just discussed, most evidence seems now in favor of a strong influence of the a -axis lattice parameter on the intrinsic $T_c(p)$, as is also expected from Hubbard models, see e.g. the work of Angilella et al. [38]. The experimental work by Tang et al. [39] shows a very nice correlation between T_c and a (we use a, b, c to indicate the lengths of the a, b, c -axis lattice parameters). Loquet et al. [40] even find a doubling of T_c in thin films that are strained along a . Also thermal expansion and uniaxial compression experiments indicate that in-plane compression is important for $T_c(p)$ (see e.g. Table 1 of Ref. [40]). In particular, Kierspel et al. [41] find for the intrinsic pressure dependence for pressure along c practically no effect and for in-plane pressure a value of $dT_c/dp \simeq 0.9 \text{ K/GPa}$, which is close to the intrinsic value as determined above for $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_7$ and to that of Ref. [23].

On the other hand, doping is closely connected to the c -axis lattice parameter. For example, Meingast et al. [42] show that dT_c/da and dT_c/db are not very sensitive to doping while dT_c/dc is large for underdoped samples and about zero for optimally doped samples. Also Presland et al. [36] find that c depends on annealing conditions (i.e. different doping), while a is constant. Also they point out that $\partial T_c / \partial c < 0$ for the under stoichiometric conditions underdoped ($n = 3$) $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, while $\partial T_c / \partial c > 0$ for the under stoichiometric conditions overdoped ($n = 2$) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

Hence, there is quite some evidence that c mainly influences doping, while a mainly influences the intrinsic T_c . Of course, there is an interplay between these two effects and the exact nature of the block layers is also important in determining T_c , as is evident from the difference in maximum

T_c values between e.g. $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$.

We arrive at the following tentative scenario for $T_c(p)$. Under pressure the block layers approach the CuO_2 layers and the hole doping increases. If the layer is originally underdoped, this enhances T_c ; if it is overdoped, it decreases T_c . At the same time an intrinsic effect possibly related to in-plane (a -axis) compression enhances T_c (at least a low pressure). The resulting T_c of the compound is determined by the sum of these effects on the various CuO_2 layers.

Now the various curves of Fig. 1 will be discussed.

For the underdoped $\text{YBa}_2\text{Cu}_4\text{O}_8$, pressure both increases doping and the intrinsic T_c leading to a spectacular increase of T_c under pressure by nearly 30 K. The $T_c(p)$ curve is asymmetric and bell shaped, which is fully consistent with a parabolic $T_c(n_h)$ curve and a weakly increasing intrinsic $T_c(p)$. The compound $\text{YBa}_{1.85}\text{La}_{0.15}\text{Cu}_4\text{O}_8$ behaves in a similar way.

By contrast, $\text{YBa}_2\text{Cu}_3\text{O}_7$ is close to optimal doping, the effect of pressure-induced doping on T_c is hence small and the main contribution to $T_c(p)$ is the intrinsic effect, leading to the observed weak increase of $T_c(p)$. As explained above, the observed behavior of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ is just a proximity coupling average between $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$. In the macroscopically tetragonal superconductor $\text{CaLaBaCu}_3\text{O}_7$, the chains are fragmented and charge transfer between the chains and CuO_2 layers is frustrated as found from our $H_{c2}(p)$ measurements [43]. Hence, the observed $T_c(p)$ is only due to the intrinsic $T_c(p)$ and dT_c/dp is very modest. At ambient pressure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is already overdoped and increasing n_h by pressure quickly brings down its T_c even further [44]. In the underdoped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ a positive dT_c/dp is observed, as expected.

The complicated behavior which may result from the presence of inequivalent CuO_2 layers in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ and $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10}$ was already discussed above.

In fact, we investigated samples of different origin of the two mercury compounds, and the results are somewhat different [34]. Our highest T_c for

$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ is 146.5 K (here and here only we use the definition for T_c of Ref. [27]), which is much lower than the reported [27] maximum of 164 K. Since our work [34] on high quality, pure samples of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ and $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10}$ does not yield such high values, we can only conjecture about the origin of the observed 164 K. Future high-pressure experiments may give further insight and thus may open the way to even higher T_c values.

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