

Superconductivity at 133 K in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ under high pressure

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The pressure dependence of the superconducting transition temperature T_c of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (Tl-2223) has been measured under pressures up to 13 GPa (130 kbar). At 4.2 GPa a maximum is observed with a T_c of 133 K. This is the highest T_c yet observed for any high- T_c superconductor with the exception of the recently discovered mercury-based compound $\text{Hg-Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ (Hg-1223). Because of some structural differences between Tl-2223 and Hg-1223, a slightly higher maximum T_c is predicted for Hg-1223. Both T_c and its pressure dependence are discussed on the basis of a simple charge-transfer model.

A characteristic feature of all high- T_c superconductors is their layered structure containing CuO_2 layers which are essential for the occurrence of superconductivity in these materials and which also determine to a large extent their normal-state properties. As an example the structure of Tl-2223 is shown schematically in fig. 1(a). In high- T_c superconducting cuprates the number n of adjacent CuO_2 layers generally ranges from 1 to 4, and occasionally even $n=5$ or 6 intergrowths are observed. Compounds with $n>2$ are particularly interesting because the CuO_2 layers are topologically inequivalent: e.g. in Tl-2223, an $n=3$ compound, there are two outer CuO_2 layers (o) and one inner CuO_2 layer (i) in each half-unit cell. For the thallium-based compounds the highest T_c values are found in precisely this $n=3$ structure. In this study the work of Berkley et al. [3] on Tl-2223 is extended to higher pressures.

Enhancement of T_c in a particular compound depends largely (but not solely, see below) upon optimization of the hole concentration n_h , i.e. the number of holes in the CuO_2 layers per Cu atom. Both from chemical substitution [4] and from high-pressure experiments [5] on superconducting cuprates there is much support for the notion that T_c has an

approximately parabolic dependence upon n_h : $T_c = T_{c \max} [1 - \beta(n_h - n_{h \max})^2]$ with $\beta \sim 40$ and $n_{h \max} \simeq 0.2$. The actual values of β and $n_{h \max}$, and in particular that of $T_{c \max}$, may vary from one compound to another and are probably related to structural differences, which for instance determine the charge distribution between and within the CuO_2 layers and the coupling between adjacent CuO_2 layers.

Optimization of n_h and hence T_c can be done either by chemical substitution, by controlling the oxygen stoichiometry, or sometimes more easily and in a continuous way, by high pressure. In this work high pressure is used.

Pressure is applied at room temperature using a cryogenic diamond anvil cell made of beryllium copper alloy (Berylco 25) and is determined for each run near the superconducting transition temperature by measuring the pressure-induced shift of the R_1 fluorescence line of ruby, of which small pieces are pressurized together with the sample. The calibration given by Mao et al. [6] to determine the pressure is used after correction for the temperature dependence of the ruby R_1 line. The temperature is

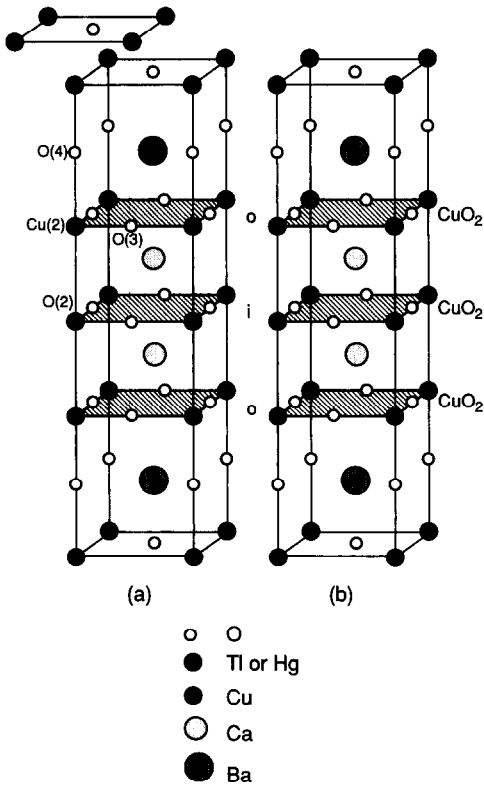


Fig. 1. Schematic representation of the idealized structures of (a) Tl-2223 and (b) Hg-1223. Striking is the strong resemblance between these two compounds. The unit-cell dimensions for Tl-2223 and Hg-1223 are, respectively, $a=3.85 \text{ \AA}$, $c=35.88 \text{ \AA}$ (see ref. [1]) and $a=3.85 \text{ \AA}$, $c=15.95 \text{ \AA}$ (see ref. [2]).

measured using a standard Pt-100 resistor mounted near the diamonds.

The superconducting transition is determined resistively. By means of a specially developed technique [7] six gold wires are connected to the 300 μm diameter sample. The resistance of the sample as a function of temperature $R(T)$ is measured using only four wires (the other two are spares) in a standard four-probe configuration under quasi-hydrostatic pressure up to 13 GPa. In fig. 2 typical resistance curves at 1.9 GPa, 4.4 GPa and 9.4 GPa are shown. For samples with such a sharp resistive transition the transition temperature T_c is conveniently defined as the intersection of the tangent through the inflection point of $R(T)$ at the transition with a straight-line fit of the normal state just above the transition.

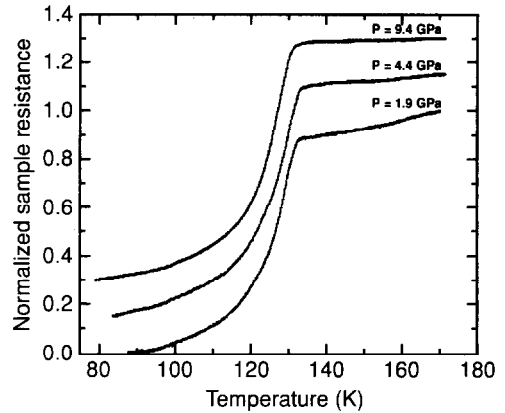


Fig. 2. Typical resistance curves of Tl-2223 at 1.9 GPa, 4.4 GPa and 9.4 GPa. The curves are normalized with respect to the resistance values measured at around 170 K. For clarity the curves are shifted by an amount of 0.15 with respect to each other.

The Tl-2223 sample investigated in this experiment consists of a single grain taken from batch L398A [8] which is of composition $\text{Tl}_{1.6}\text{Ba}_2\text{Ca}_{2.4}\text{Cu}_3\text{O}_{10+x}$ and has a zero-resistance temperature of 119 K as synthesized. The batch is vacuum annealed in a sealed quartz tube at low temperature in order to increase T_c . As determined by X-ray and neutron diffraction the Tl-2223 sample is single phased before and after annealing. Following this annealing a weight loss of almost 5% is measured with respect to the as-sintered material. Liu et al. [8] propose that thallium loss is the major contributing factor, thus increasing the number of holes in the Tl-2223 phase. The hole concentration is furthermore optimized by annealing in oxygen afterwards. The highest T_c at ambient pressure reached in this way is 128.5 K. Zero resistance (within the resolution of the equipment used) occurs at 125.1 K. Loading additional oxygen in a similarly prepared sample results in a small decrease in T_c indicating that the sample is indeed optimally doped when T_c is 128.5 K. This is confirmed by thermopower measurements before and after annealing. For the sample with the highest T_c the thermopower just above T_c is 7 mV/K and at room temperature 2 mV/K, almost identical to other high- T_c superconductors at optimum doping [9].

In fig. 3 T_c is given as a function of pressure up to 13 GPa (included are also the results of Berkley et

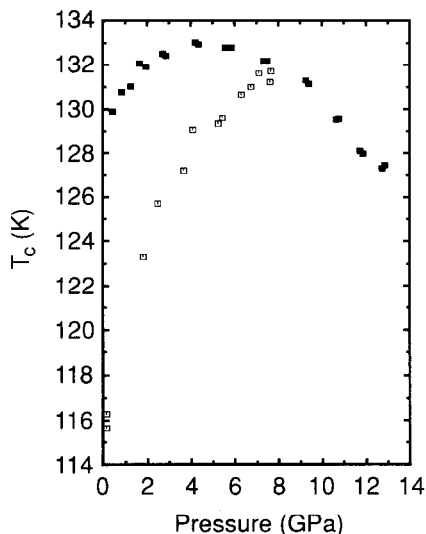


Fig. 3. The critical temperature T_c of Tl-2223 as a function of pressure up to 13 GPa determined from resistance curves of which some are shown in fig. 2 (■). Included are also the results of Berkley et al. [3] (□).

al. [3]). After a relatively large initial increase at a rate of 1.75 K/GPa, the pressure dependence of T_c diminishes and T_c reaches a maximum value of 133 K at 4.2 GPa. A further increase of pressure results in a lowering of T_c . This maximum value is the highest critical temperature reported so far for any high- T_c superconductor with the exception of Hg-1223. This compound with an ambient T_c of 133 K was recently discovered by Schilling et al. [10] while Gao et al. [11] not only confirmed this but also observed a slight increase in T_c up to their highest pressure of 1.7 GPa. The roughly parabolic $T_c(P)$ behavior of Tl-2223 is consistent with the parabolic $T_c(n_h)$ dependence mentioned above and a linear increase of n_h with pressure as is measured [12] on $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) and probably holds for most high- T_c superconductors [5].

The virtually identical values of T_c for Tl-2223 under pressure and for Hg-1223 raises interesting questions about the relationship between the T_c 's of these compounds and their structures. From the outset it is evident that this can only be discussed by drawing analogies with other superconducting systems. In this context it is most instructive to consider the $n=2$ compounds. Very interesting is that a common maximum T_c of 100–110 K is reached in many of these

compounds. For example, in high-pressure experiments on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123) T_c increases from 95 K at ambient pressure to 107 K at 14.9 GPa [13], while on an oxygen-deficient Y-123 sample with a T_c around 70 K Berman et al. [14] observed a maximum T_c above 100 K at 14.0 GPa. Even in Y-124 the T_c of 79 K at ambient pressure is exceeded by almost 30 K to reach 108 K at a pressure of 12 GPa [7,12]. In chemically substituted Y-124, where Ca is substituted for Ba and Y, T_c can be increased from 90 K to 99 K by applying a pressure of 8.8 GPa as shown by Van Eenige et al. [15].

In chemical substitution experiments on $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_{7+x}$ (Tl-1212 phase) where Y is substituted for Ca [16,17] also a maximum T_c of 108–110 K is observed. A still higher T_c is found in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+x}$ (Tl-2212) which has a maximum T_c of 119.5 K at 1.9 GPa [18]. These examples show that pressure is a powerful means to optimize T_c and that within a class of materials high-pressure optimization of T_c leads virtually to the same maximum T_c (i.e. $T_{c \text{ max}}$). By analogy it is thus expected that the 133 K found in this work for Tl-2223 corresponds to $T_{c \text{ max}}$ of the $n=3$ thallium-based compounds. The question is then whether or not $T_{c \text{ max}}$ for the $n=3$ mercury-based compounds will be higher. To try and answer this question the structures of Tl-2223 and Hg-1223 have to be compared first (see fig. 1). Both compounds have identical perovskite units $[-\text{BaO}-\text{CuO}_2-\text{Ca}-\text{CuO}_2-\text{Ca}-\text{CuO}_2-\text{BaO}-]$ and differ only in their respective Tl_2O_2 and HgO_x layers, which separate the perovskite blocks and act as charge reservoirs from which charge can be transferred to the CuO_2 layers. Provided that an optimal hole concentration can be achieved in Hg-1223 any differences between these compounds must be (indirectly) attributable to these charge-reservoir layers.

It has been proposed that the distribution of n_h between the copper (Cu(2)) and oxygen (O(2) and O(3)) sites in the CuO_2 layers is an important factor in determining $T_{c \text{ max}}$, although experimentally not readily accessible. This distribution has variously been expressed in terms of Madelung site potentials [19], copper NQR frequency [20] or bond-valence sums [21]. Generally, for high- T_c materials $T_{c \text{ max}}$ is larger if the fractional coordination of Cu(2), O(2) and O(3) are reduced [21]. Thus, provided that n_h

is maintained at the optimum level, $T_{c \text{ max}}$ increases as the a -lattice parameter, the Ba–(O(2), O(3)) and the Cu(2)–O(4) (apical oxygen) bond lengths increase. Above, the change of T_c with pressure was attributed to a change in n_h . This is of course an oversimplification, since many other factors may affect T_c if pressure is increased. In particular the experimental fact that T_c continues to rise with pressure for the apparently optimally doped (at ambient pressure) Tl-2223 sample implies that either $T_{c \text{ max}}$ increases with pressure or the charge distribution between the inequivalent CuO_2 layers becomes more uniform. The maximum T_c for a compound containing inequivalent CuO_2 layers, each of them obeying a parabolic phase diagram, is highest when the individual CuO_2 layers reach their maximum T_c at the same pressure, or oxygen concentration. This results directly from the proximity coupling of these layers [22]. Because pressure reduces all of the bond lengths the observed elevation of T_c with pressure to 133 K probably arises not from an increased $T_{c \text{ max}}$ but from an increasingly uniform charge distribution. Total electron-energy minimization calculations [23] show that this is possible and likely.

Due to the short bond length of the two-coordinated mercury atom and the almost complete absence of oxygen in the mercury layer which diminishes the (O(2), O(3))–O(4) repulsion, the Cu(2)–O(4) bond length (between the CuO_2 layer and the apical oxygen) is larger for Hg-1223 (see ref. [2]) than for Tl-2223 (see ref. [1]). As a consequence a slightly higher $T_{c \text{ max}}$ is expected for the mercury-based compound, because the larger Cu(2)–O(4) bond length implies a more uniform charge distribution between the two kinds of inequivalent CuO_2 layers and the tendency for the inner CuO_2 layer to be overdoped relative to the outer layers will be diminished.

Although originally claimed to be of major importance for high- T_c superconductivity, the coupling between adjacent CuO_2 layers does not seem to be very important for the determination of T_c [22]. In any case it is unlikely that it would be a major factor determining the difference between Hg-1223 and Tl-2223.

To investigate the behavior of the $n=4$ compounds the pressure dependence of T_c in $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12+x}$ (Tl-2234) has been measured

[24] also and a $T_{c \text{ max}}$ of 120 K is found at 6.6 GPa. Calculations indicate a very non-uniform distribution of charge between the inner and outer CuO_2 layers in this compound [23]. In light of the arguments given above this non-uniform distribution is probably the principal reason for the decrease of $T_{c \text{ max}}$ with respect to the value found for Tl-2223. Because of the longer Cu(2)–O(4) bond length in the mercury-based compounds again a higher $T_{c \text{ max}}$ is expected for $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+x}$ (Hg-1234) reflecting a more uniform charge distribution.

In conclusion, the pressure dependence of the superconducting transition temperature in Tl-2223 is determined. An initial increase of 1.75 K/GPa and a $T_{c \text{ max}}$ of 133 K at 4.2 GPa are found. This is the highest transition temperature yet observed in a thallium-based superconductor and is virtually identical to that currently observed in the new Hg-1223 compound. By analogy with the $n=2$ compounds and on the basis of structural differences known so far it is expected that $T_{c \text{ max}}$ for Hg-1223 will be slightly higher than that for Tl-2223.

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Note added in proof

After completion of this manuscript, Chu et al. [25] and Nuñez-Regueiro et al. [26] reported to have increased the T_c of Hg-1223 up to 155 K by applying, respectively, 15 GPa and 23.5 GPa of pressure. This very important result is consistent with the discussion given above. The relative increase in T_c due to pressure ($\sim 17\%$) is almost identical to that observed in Y-123 [13]. For a further discussion on the increase of $T_{c \text{ max}}$ under pressure see ref. [27].

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