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Pressure dependence of the superconducting transition temperature in single crystals of $Tl_2Ba_2Ca_2Cu_3O_{10-x}$

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The pressure dependence of the superconducting transition temperature, $T_c(P)$, has been measured in single crystals of $Tl_2Ba_2Ca_2Cu_3O_{10-x}$. In two overdoped samples, $T_c(P)$ is observed to increase from 116 K at atmospheric pressure to 131.8±0.5 K at 7 GPa. We believe this is the highest T_c reported to date. The initial slope, dT_c/dP, was measured to be 4.8±0.3 K/GPa. For samples with T_c's at atmospheric pressure approaching the reported optimum value for this compound of 125 K, the effect of pressure is reduced. These results are discussed in terms of existing theoretical models.

Studies undertaken to determine the response of each new class of high-T_c superconductors to pressure are often motivated by the desire to understand what modifications of the crystal lattice might be made to improve the superconducting properties of the material, especially T_c. The investigation of the $La_{2-x}Sr_xCuO_4$ by Chu *et al.*,[1] which led to the preparation of the $YBa_2Cu_3O_{7-x}$ compound and a doubling of the highest T_c achieved at the time, is cited most often in this context. The large dT_c/dP and high ambient T_c of compounds such as $YBa_2Cu_4O_8$ (Y 1:2:4) and $Tl_2Ba_2Ca_2Cu_3O_{10-x}$ (Tl 2:2:2:3) make them attractive starting materials for investigators interested in pushing T_c even higher.

Here we present the results of our measurements of $T_c(P)$ on single crystals of $Tl_2Ba_2Ca_2Cu_3O_{10-x}$ to 7.5 GPa. We have measured what we believe are the highest superconducting transition temperatures reported to date. The total change in $T_c(P)$ from ambient conditions to the highest applied pressure was observed to be greater than 15 K.

Crystals were prepared from a mixture of Tl_2O_3, BaO_2, CaO_2, and CuO of composition [Tl]:[Ba]:[Ca]:[Cu] = 2:2:3:4 which was placed in a gold capsule and heated according to the following protocols for each of the four samples. Samples A and C were heated in 4 h to 917 °C, maintained for 3 h at 917 °C, and cooled in 12 h to 695 °C; the furnace was then turned off and the samples removed at 350 °C. Sample B was heated in 9 h to 920 °C, maintained for 3 h at 920 °C, cooled at 5 °C/h to 800 °C, and cooled in 12 h to ambient. Sample D was heated in 1.5 h to 920 °C, maintained for 3 h at 920 °C, and cooled in 7 h to 750 °C; the furnace was then turned off and the sample removed at 350 °C.

X-ray analyses of the batch of material containing samples A and C indicated a mixture of the thallium cuprate "2:2:2:3" and "2:2:1:2" phases in a ratio of approximately 60:40. Samples B and D were individually analyzed with x rays and found to contain only the "2:2:2:3" phase to the resolution of the measurement.

Pressure was applied to the crystals using a diamond anvil cell[2] constructed of fully hardened beryllium copper. The diamonds were mounted on tungsten carbide platforms, fitted with holes for optical access to the diamonds. Annealed inconel was used as the gasketing material. The pressure chamber was initially a right circular cylinder, 50 μm high and 300 μm in diameter. A typical pressure run would result in about a 50% reduction in the gasket thickness. The crystals were in the shape of rectangular solids with typical dimensions of $200 \times 100 \times 15$ μm. Post-run visual analyses of the crystals showed them to be undamaged by the high-pressure environment. In one instance, this was further confirmed by x-ray-diffraction measurements.

A 4:1 methanol:ethanol mixture was used as a hydrostatic medium. The pressure in the sample environment was measured *in situ* using the ruby fluorescence technique.[3,4] A zero-pressure reference value was obtained at the same temperature as the sample by measuring the position of the $R1$ line from a ruby chip glued to the cell housing outside of the sample space. Because of differences in the thermal expansivities of the constituent parts of the cell, the pressure can increase as the temperature is reduced. For this reason the pressure was measured within ±10 K of T_c.

Pressures were increased at room temperature by manual advancement of the piston diamond against the stationary diamond. The hydrostatic pressure environment insured by the fluid in the cavity was frozen in as the cell was cooled. Thus, the only shear stresses to which the samples might be exposed would be those arising during the solidification of the fluid.

The T_c of each sample was determined by monitoring the ac magnetic susceptibility of the pressure cavity. A 50-turn primary coil and a 250-turn secondary coil were each wound closely around the perimeter of the stationary diamond. The primary was driven by a 2-kHz sine wave which produced a field at the sample of about 2 G. A Hartshorn bridge and lock-in arrangement were employed to measure the in- and out-of-phase response of the coil. When the background signal due to the susceptibilities of the gasket and the coils was subtracted from the measured signal, the superconducting transition of the sample was clearly observed. However, the small filling factor of the sample in the coil precluded quantitative comparison of the sample susceptibility and output signal. It was observed that the output response of the sample diminished at higher pressures.

As an illustration of how the transition temperature is obtained, the susceptibility, $\chi(T)$, is shown in Fig. 1. The measurement is made at selected pressures to the maximum applied pressure of 7.5 GPa. The zero-pressure susceptibility shown in Fig. 1 was measured using a large crystal, from which a small piece was obtained for the high-pressure measurements. The amplitude of the transition of the zero-pressure measurement is, therefore, much larger than that from the smaller crystal used at high pressures. These curves have been obtained by creating a linear fit to $\chi(T)$ for $T > T_c$ and subtracting this from the raw data. The value of T_c is taken to be the onset of superconductivity defined by the intersection of a line drawn through the steep slope of the curve and the region of zero slope above the transition. Note that a second phase transition becomes prominent as the pressure is increased. An apparent phase separation has also been observed in susceptibility studies of the Tl 2:2:1:2 compound at pressures above 6 GPa.[5]

In Fig. 2, $T_c(P)$ is plotted for samples A and B. They have ambient T_c's of 115.9±0.5 K and 116.5±0.5 K, respectively. For sample A T_c increased to 131.8±0.5 K at 6.9 GPa, the highest applied pressure. Sample B behaves similarly, T_c increased to 131.5±0.5 K at 7.4 GPa. The initial slope of dT_c/dP is 4.8±0.3 K/GPa, which is twice the value recently reported for the "2:2:1:2" stoichiometry of the thallium family.[6] A trend toward saturation of the transition temperature at pressures above 7.5 GPa is apparent from the data in Fig. 2. Pressures greater than 7.5 GPa exceed the capabilities of the apparatus used in this work. Due to the irreversible deformation of the gasket, it is not possible with the apparatus used here to monitor $T_c(P)$ as the pressure is released. However, T_c(1 atm) was measured at the start and end of each pressure run and found to be unchanged.

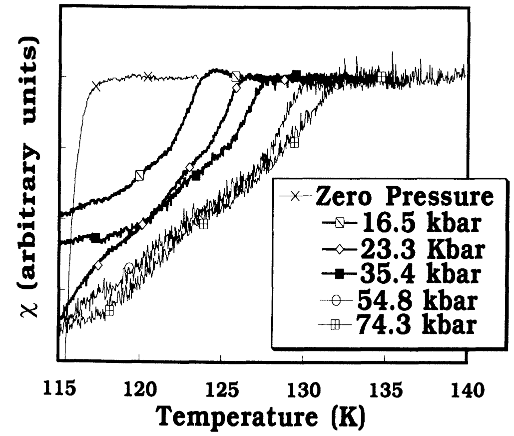

FIG. 1. ac magnetic susceptibility, $\chi(T)$, of Tl 2:2:2:3 single crystal, sample A, at selected pressures up to about 7.5 GPa. The curves measured under pressure are those of a small piece of the crystal used to obtain the zero-pressure curve.

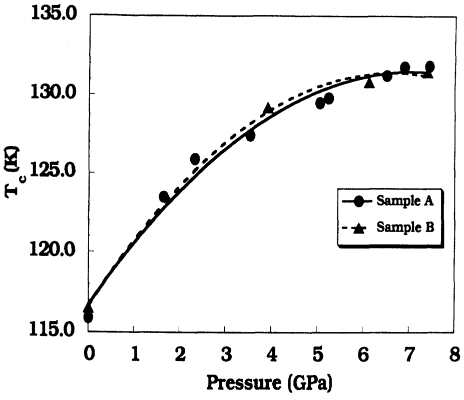

FIG. 2. T_c dependence on pressure for two single-crystal samples of the Tl 2:2:2:3 superconductor with ambient T_c's of about 116 K.

In Fig. 3, $T_c(P)$ is plotted for samples C and D. They have ambient T_c's of 124.5±0.5 K and 121.3±0.5 K, respectively. They are much closer to the maximum value of 125 K reported for the stoichiometric Tl 2:2:2:3 compound than those of samples A and B. For samples C and D, $T_c(P)$ rises very slowly at a rate of about 0.7 K/GPa. In both cases, a turnover is observed and is reminiscent of the behavior of the turnover seen in the Tl 2:2:1:2 materials.[5]

From Figs. 2 and 3, it is apparent that the behavior of $T_c(P)$ for these samples is correlated quite strongly with the ambient T_c. Samples A and B have identical T_c's to within 1 K and exhibit a nearly identical dependence on pressure. This is so even though they were selected from two different crystal batches. Samples A and B follow the behavior commonly observed in the high-T_c materials in which a depressed ambient T_c is accompanied by a large dT_c/dP. This tends to drive T_c to a value which

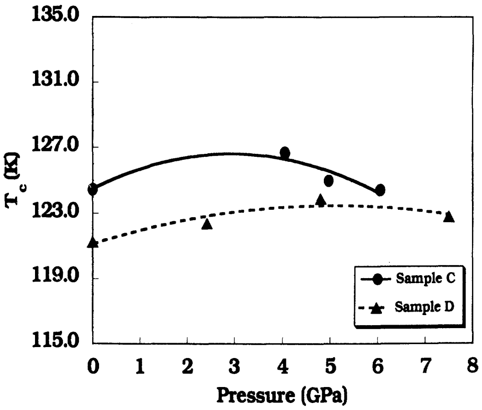

FIG. 3. T_c dependence on pressure for two single-crystal samples of the Tl 2:2:2:3 superconductor with ambient T_c's of 121.3 and 124.5 K. These are closer to the nominal optimum value of 125 K than the samples of Fig. 1.

exceeds the nominal optimum value by a considerable margin. For the samples measured here, 6.5 K was gained in T_c at the highest pressures available to us, 7.5 GPa. In an analogous fashion, the Y 1:2:4 material responds to pressure with a larger increase in T_c for oxygen-deficient samples.[7] Samples C and D, on the other hand, have ambient T_c's much closer to the optimum T_c for the compound and are observed to have a slope dT_c/dP which is seven times smaller than the other pair of samples.

Previous investigations of the Tl 2:2:2:3 material have been limited to the use of sintered ceramic samples. In a recent study,[8] a dT_c/dP of 5.0 K/GPa for ceramic Tl 2:2:2:3 samples with a T_c of 100 K was obtained. The transition temperature increased to 103 K upon application of the maximum applied pressure of 1.0 GPa. In another experiment,[9] a dT_c/dP of 1.2 K/GPa was measured for ceramic samples with a T_c of 106 K. Upon application of 20 GPa, the transition temperature increased to 113 K and appeared headed toward saturation. The T_c's of the material used in both of these investigations are much lower than those achieved in higher-quality material of the Tl 2:2:2:3 phase. In both studies, T_c increased monotonically throughout the range of applied pressures, in agreement with the behavior of the lower-T_c samples of the present work, with no observed turnover toward negative dT_c/dP. This behavior is unlike that of the Tl 2:2:1:2 phase for which a broad but clear maximum in T_c between 2 and 4 GPa has been reported.[5,10]

The precise mechanism for the effect of pressure on T_c in these materials is not yet understood. In general, the high-T_c superconductors can be distinguished by the positive dT_c/dP observed in the hole-doped materials and negative dT_c/dP observed in the electron-doped materials.[11] Of the hole-doped superconductors, only the $Tl_2Ba_2CuO_8$ (Tl 2:2:0:1) and $Y_{1-y}Pr_yBa_2Cu_3O_{7-x}$ (Pr 1:2:3) exhibit a negative dT_c/dP which, along with the T_c, is strongly dependent upon the oxygen concentration.[12,13] In general the hole-doped superconductors exhibit positive dT_c/dP's regardless of the initial state of oxidation of the material.[14]

$YBa_2Cu_3O_{7-x}$ and $La_{2-x}Sr_xCuO_4$ are observed to have an optimum carrier concentration at which T_c is maximum under ambient conditions.[15,16] Since Hall-effect measurements indicate that applied pressure increases the carrier concentration in these materials,[12] dT_c/dP would be expected to be negative for samples which are overdoped, a condition easily satisfied by a number of materials including those of the present study, and positive for samples which are underdoped. In the overdoped case, the pressure pushes the material away from the optimum carrier density; in the underdoped case, pressure moves the carrier density toward the optimum value. T_c then falls or rises, respectively.

In the case of the present study, lower-T_c samples such as A and B are thought to be overdoped with oxygen with respect to those observed with higher T_c's. This assumption is made in light of work[17,18] which has shown that T_c for this material can be elevated to the optimum ambient value by removing oxygen from the superconductor by hydrogen reduction. If the material is truly overdoped, T_c would be expected to decrease with pressure, which is contrary to the observation.

On the other hand, one can adopt the picture of Kresin and Morowitz[19] which was recently offered as a possible explanation[5] for the behavior of $T_c(P)$ in the Tl 2:2:1:2 system. In this scenario, the Fermi wave vector is given as $k_F = \sqrt{2\pi nc}$ where n is the carrier concentration and c is the spacing between weakly coupled two-dimensional conducting systems, i.e., the Cu-O planes. T_c is optimized when k_F is equal to some value, q_c. For values of k_F above and below q_c, T_c decreases. This implies that n and c have equal weight in controlling k_F. If pressure is applied to the sample and $k_F > q_c$ (overdoped), c will decrease with pressure, reducing k_F closer toward q_c, and increasing T_c. This assumes, of course, that n does not increase with pressure, or at least increases more slowly than c.

Finally, in an exhaustive review by Schilling and Klotz,[20] the dependence of T_c on carrier concentration and pressure is examined for a large collection of experiments and high-T_c material systems. They conclude that the observed behavior cannot be explained in terms of the carrier concentration alone and probably requires an understanding of the effect of pressure on the dynamics of the crystal lattice as well.

In conclusion we have measured superconducting transition temperatures as high as 131.8±0.5 K at pressures of 7.5 GPa in overdoped single-crystal samples of the thallium "2:2:2:3" superconductor. These T_c's appear to be the highest obtained to date. As expected, the effect of pressure on T_c of samples with ambient T_c's close to the optimum value is considerably smaller than for samples which are overdoped. This result may suggest an appropriate protocol for raising the ambient T_c higher still in overdoped samples by a suitable chemical substitution.

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