Enhancement of the Critical Temperature of HgBa2CuO4+δ by Applying Uniaxial and Hydrostatic Pressure: Implications for a Universal Trend in Cuprate Superconductors

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It is well known that the superconducting transition temperature ($T_c$) of cuprate superconductors can be enhanced by varying certain structural and electronic parameters, such as the flatness of the CuO2 planes or their doping level. We determine the uniaxial and hydrostatic pressure derivatives of $T_c$ in the structurally simple tetragonal compound HgBa2CuO4+δ near optimal doping. Our results provide experimental evidence for two further methods to enhance $T_c$: (i) reducing the area of the CuO2 planes, and (ii) increasing the separation of the CuO2 planar groups. $T_c$ is found to couple much more strongly to the ratio $c/a$ of the lattice constants than to the unit cell volume. A comparison with prior results for structurally more complicated cuprates reveals a general trend of uniaxial pressure derivatives with $T_c$.

One of the most important goals in research on the high-$T_c$ cuprates [1–3] is to establish those parameters which, when judiciously varied, lead to an increase in the value of $T_c$. The critical temperature in all high-$T_c$ cuprates approximately follows an inverted parabolic shape as a function of hole (or electron) doping, reaching a maximum value, $T_c^{\text{max}}$, at optimal doping. This maximum value, however, varies considerably between the different cuprate compounds. In single-layer cuprates, $T_c^{\text{max}}$ varies between $\sim 30$ K for La2−xBaxCuO4 [4] and $97$ K for HgBa2CuO4+δ (Hg-1201) [2]. An important goal is to identify the parameters which determine these large differences, because such knowledge can in principle be used to further optimize $T_c^{\text{max}}$ and may provide clues about the mechanism(s) responsible for the superconductivity.

In the optimally doped three-layer compound HgBa2Ca2Cu3O8+δ (Hg-1223), where $T_c \approx 134$ K, $T_c$ has been shown to initially increase under hydrostatic pressure at the rate $dT_c/dP \approx +1.75(3)$ K/GPa [5], reaching a value near 160 K at 30 GPa [6]. In fact, for all optimally doped cuprates with $T_c$ values of 90 K or more, $dT_c/dP$ lies between $+1$ to $+2$ K/GPa [3]. However, it is unclear which of the various parameters or features which vary under pressure (the area, separation, or flatness of the CuO2 planes, the carrier concentration in the planes, etc.) is mainly responsible for this rate of increase in $T_c$. In order to obtain such information, the uniaxial pressure derivatives $dT_c/dP_i$ must be determined. Previous experiments on two optimally doped cuprates with orthorhombic structure, La2−xSr1xCuO4 (La-214) [7] and Bi2Sr2CaCu2O8+δ (Bi-2212) [8], revealed that $dT_c/dP_c$ is negative and larger in magnitude than the positive derivatives $dT_c/dP_a$ and $dT_c/dP_b$. In contrast, studies by Meingast et al. [9] and Welp et al. [10] on detwinned, optimally doped YBa2Cu3O6.95 (Y-123) demonstrated that $dT_c/dP_a$ and $dT_c/dP_b$ are nearly equal in magnitude, but opposite in sign, $dT_c/dP_c$ being negligible. In order to better understand these seemingly contradictory results and to search for possible universal behavior, it is essential to investigate structurally simple tetragonal cuprates for which only two partial derivatives, $dT_c/dP_a$ and $dT_c/dP_c$, need be considered. The Hg compounds with one, two, and three CuO2 layers, which are tetragonal and exhibit the highest known values of $T_c$, would appear to be ideal for in-depth studies under both uniaxial and hydrostatic pressure [2]. For Hg-1201 sizable, high-quality single crystals have recently become available [11] and have enabled, for example, the clear observation of a novel type of magnetic order below optimal doping [12].

In this Letter we determine the uniaxial and hydrostatic pressure derivatives of $T_c$ for single-layer Hg-1201 at nearly optimal doping. We find that $T_c^{\text{max}}$ is enhanced both by reducing the area of the CuO2 planes and by increasing the separation of the planar groups, i.e., by increasing the ratio $c/a$ of lattice constants. Comparison with results for other cuprates near optimal hole doping reveals a universal trend of the planar and c-axis partial derivatives with the $T_c$. We conclude that the behavior...
of Y-123 is unusual and not representative of the cuprates.

The Hg-1201 single crystal was (nearly) optimally doped by a heat treatment in air at 350 °C for ~30 days [11]. The thermal expansion was measured in two different homemade capacitance dilatometers with a typical relative resolution of $\Delta L/L = 10^{-8} - 10^{-10}$. Data were taken upon heating at constant rates of 15–20 mK/s. The data shown in Fig. 2(a) were obtained on a fairly large crystal with dimensions of 5 and 0.8 mm along the $a$ and $c$ axes, respectively. For the measurements shown in Fig. 2(b) with and without magnetic field, a smaller part of the crystal was used; to enhance the signal/noise ratio, the data shown represent the average over ten experimental runs. Details of the He-gas techniques used are given elsewhere [13].

The results of the present ac susceptibility measurements on an optimally doped Hg-1201 single crystal with mass 0.7 mg (density $7.0 \text{ g/cm}^3$) under hydrostatic (He-gas) pressure are shown in Fig. 1 (inset). The transition is seen to be quite sharp, with 10%–90% transition width $\Delta T_c = 0.3 \text{ K}$ and a magnitude consistent with full shielding; no correction is made for the demagnetization factor. The application of 0.69 GPa pressure at ambient temperature is seen to shift the superconducting transition to higher temperature by 1.06 K. The pressure was then reduced consecutively to 0.42 GPa at 170 K, to 0.21 GPa at 100 K, and finally to 0 GPa at 140 K.

A plot of $T_c$ versus pressure for these five measurements is shown in Fig. 1. The value $T_c \approx 94.85 \text{ K}$ at ambient pressure is determined from the transition midpoint; the $T_c$ values at high pressure are determined relative to this value from the respective shift in the entire superconducting transition curve. $T_c(P)$ is seen to be a reversible function of pressure, independent of the temperature at which the pressure is changed. A linear least-squares fit to the reversible $T_c(P)$ dependence in Fig. 1 yields the straight dashed line with slope $dT_c/dP = +1.48(5) \text{ K/GPa}$. A superior fit (solid line) is achieved through the quadratic equation $T_c(K) = 94.85 + 1.21(8)P + 0.49(13)P^2$, where $P$ is in GPa. The initial slope is thus $dT_c/dP = +1.21(8) \text{ K/GPa}$.

In Fig. 2(a) the individual thermal expansion coefficients $\alpha_a$ and $\alpha_c$ for a Hg-1201 crystal along the $a$- and $c$-axes, respectively, are plotted versus temperature and compared to both their difference ($\alpha_a - \alpha_c$) and one-third of the calculated volume expansion coefficient. The data show small positive and negative anomalies in the $a$ and $c$ axes at $T_c = 95 \text{ K}$, respectively, which become more evident in ($\alpha_a - \alpha_c$) because of their opposite sign.

In order to obtain accurate values of partial pressure derivatives using the Ehrenfest relation, one needs reliable values for both the jumps at $T_c$ in the specific heat $\Delta C_p$ and

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**FIG. 1** (color online). $T_c$ versus pressure from susceptibility data in inset. Numbers give order of measurement. See text for details. (inset) Real part of ac susceptibility at 0.1 Oe and 1023 Hz versus temperature for single-crystalline Hg-1201 at different hydrostatic (He-gas) pressures.

**FIG. 2** (color online). (a) Temperature-dependent linear thermal expansion coefficients $\alpha$ along the $a$ and $c$ axes for tetragonal Hg-1201 crystal at 0 T magnetic field. Dashed vertical line marks superconducting transition. (b) Change in temperature-dependent expansion coefficients $\alpha_i$ and scaled specific heat $C_p$ data (solid black curves) from Ref. [14] in 0 and 10 T magnetic field.
in the individual thermal expansivities $\Delta \alpha_i$. In the high-\(T_c\) cuprates, the anomalies in \(C_p\) are quite small in comparison to the phonon component, making it difficult to isolate the electronic component: furthermore, the jumps at \(T_c\) are not of the simple mean-field type, but rather of the \(\Lambda\)-type due to the strong superconducting fluctuations \cite{14,15}. These considerations are especially true for Hg-1201, making an application of the Ehrenfest relation difficult.

Following the work of van Heumen et al. \cite{14}, we have overcome this problem by making use of the fact that for the cuprates the superconducting signature in the specific heat, and thus also the thermal expansivity \cite{15}, is strongly suppressed in high magnetic fields, whereas the phonon background is unaffected. In Fig. 2(b) we plot the difference in the temperature-dependent thermal expansivity \(\alpha\) taken in both 0 T and 10 T magnetic fields. Positive and negative anomalies are now clearly seen at the superconducting transition along the \(a\) and \(c\) axes, respectively, which have shapes very similar to those in the heat capacity, whereas the transition in the thermal expansion is somewhat sharper than that in the heat capacity, due to their appreciable cancellation. Similar behavior is due to their appreciable cancellation. Similar behavior is observed for optimally doped Y-123 \cite{9,10} and Y(Ca)-123 systems \cite{16}.

From the ratio of the jumps in the thermal expansion coefficients $\Delta \alpha_i$ to that in the molar specific heat \(\Delta C_p\) at \(T_c\), the partial pressure derivatives can be derived using the Ehrenfest relation $dT_c/dP_i = (\Delta \alpha_i V_m T_c) / \Delta C_p$, where $V_m$ is the molar volume. The partial pressure derivatives of \(T_c\) are seen to be directly proportional to the jumps in the respective thermal expansivities $\Delta \alpha_i$. Therefore, from the thermal expansion data in Fig. 2(b) we can immediately conclude without further analysis that $dT_c/dP_a$ is negative and clearly larger in magnitude than the positive derivative $dT_c/dP_c$. This implies that in Hg-1201 the separation between the CuO$_2$ planes is an important factor determining \(T_c\). This result is in contrast to the findings for the optimally doped Y-123 \cite{9,10} and Y(Ca)-123 systems \cite{16} where $dT_c/dP_c = 0$ is observed.

Inserting into the Ehrenfest relation the results for $\Delta \alpha_i$ from Fig. 2(b), $V_m = 8.599 \times 10^{-5}$ m$^3$/mol, and $\Delta C_p = 4.8$ mJ/mol K, the latter value was obtained by interpolation between the 8 T and 14 T data from Ref. \cite{14}, one finds $dT_c/dP_a = +2.3(2)$ K/GPa and $dT_c/dP_c = -3.6(3)$ K/GPa. From this one can calculate the total pressure derivative $dT_c/dP = 2dT_c/dP_a + dT_c/dP_c = +1.0(7)$ K/GPa, in quite good agreement with the value $+1.21(8)$ K/GPa found above in the hydrostatic He-gas experiment.

In Fig. 3 the values of the partial pressure derivatives for the present optimally doped Hg-1201 crystal are plotted and compared to those for three other cuprate superconductors: La-214 \cite{7}, Bi-2212 \cite{8}, and Hg-1223 \cite{17}. We note that the Hg-1223 crystal that we studied was somewhat underdoped ($T_c \approx 114$ K, 20 K less than the optimally doped value) and only the partial derivative along the \(a\)-axis was measured directly, giving $dT_c/dP_a = +2$ to +3 K/GPa; the derivative along the \(c\) axis was obtained from the total hydrostatic pressure derivative $dT_c/dP = +1.5$ K/GPa by using the equation $dT_c/dP_c = dT_c/dP - 2dT_c/dP_a = -2.5$ to $-4.5$ K/GPa. These values of the partial derivatives for Hg-1223 must, therefore, be viewed as preliminary, but are quite close to those for Hg-1201. If confirmed, this would not be too surprising, since it is well known that the values of the total hydrostatic (He-gas) pressure derivative $dT_c/dP$ are, in fact, identical for Hg-1201, Hg-1212, and Hg-1223 \cite{5}.

The most important result to emerge from the present experiments is that $dT_c/dP_a$ for nearly optimally doped tetragonal Hg-1201 is negative and surpasses in magnitude the positive derivative $dT_c/dP_c$. The magnitude of the total hydrostatic pressure derivative $dT_c/dP$ is small relative to the magnitudes of the partial pressure derivatives, due to their appreciable cancellation. Similar behavior is observed for optimally doped La-214 \cite{7}, Bi-2212 \cite{8}, and Hg-1223 \cite{17}, suggesting that this is the intrinsic behavior. The results for Y-123 \cite{9,10} and Y(Ca)-123 \cite{16} are anomalous and arise from the presence of long-range CuO chains.

The present experiments imply that, once a given high-$T_c$ cuprate is doped so as to bring $T_c$ to its maximum value (optimal doping), the value of $T_c$ may be increased further by either: (i) reducing the area of the CuO$_2$ planes or (ii) increasing the separation of these planes. This could be achieved, for example, by epitaxially growing the

![FIG. 3 (color online). Partial pressure derivatives $dT_c/dP_i$ for $i = a$, $b$, and $c$ for Hg-1201 compared to those for La-214 \cite{7}, Bi-2212 \cite{8}, and Hg-1223 \cite{17}. The combined partial derivatives in the $a$ and $b$ directions are positive and seen to nearly cancel the negative derivatives in the $c$ direction. Dashed vertical lines are guides to the eye.](167002-3)
cuprate as a thin film, with the CuO$_2$ planes in the plane of the film, on a substrate with a reduced lattice parameter, thus reducing the area of the CuO$_2$ planes but increasing their separation according to Poisson’s ratio.

The question naturally arises which structural features are responsible for the $T_c$ increase when the c axis is expanded and/or the area of the CuO$_2$ planes is reduced. The fact that both the hydrostatic and uniaxial pressure derivatives of $T_c$ are so similar for the single-layer and multilayer Hg-cuprates strongly suggests that it is the separation between the CuO$_2$ planar groups, rather than the separation of the CuO$_2$ planes within a group, which is responsible for the observed increase in $T_c$ with the c axis. Jorgensen et al. [1] showed that there exists a correlation between the Cu-O apical bond distance, as well as the closely related in-plane buckling angle, and $T_c$ for two-layer cuprates. Our results are in qualitative agreement with this finding if one assumes that the Cu-O apical bond distance increases with the $c$-axis length. In fact, this was shown to be the case in hydrostatic high-pressure neutron diffraction studies [18] on Hg-1201 and Hg-1212, the Cu-O apical bond compressibility being twice that of the $c$-axis; the results for Hg-1223 were inconclusive. The role of the apical oxygen on the electronic properties has also been addressed in several theoretical works [19] which all find that $T_c^{\text{max}}$ is highest for compounds in which the apical bond distance is large.

In summary, the partial pressure derivatives of $T_c$ for Hg-1201 are found to be highly anisotropic, with $T_c$ strongly dependent on the $c/a$ lattice constant ratio, and to increase with increasing $c/a$. This result for Hg-1201 is very similar to that found previously for La-214 and Bi-2212, as well as for our preliminary results on Hg-1223, suggesting that this is the intrinsic behavior of cuprates. We also note that several other layered superconductors show similar behavior [20]. Since a valid theory for superconductivity in the cuprates should be able to predict the correct pressure dependence of $T_c$, it is hoped that the present findings will help narrow down the number of proposed mechanisms leading to high-temperature superconductivity.

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