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Volume dependence of the superconducting transition temperature for the high-temperature superconductor $HgBa_2CuO_{4+\delta}$

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The homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1, 2, 3, 4$) are the newest and most promising of the layered high-T_c superconducting materials, as demonstrated in setting the highest T_c among the known superconducting materials. The first of its series, $HgBa_2CuO_{4+\delta}$, contains only one Cu-O plane per unit cell and is superconducting with T_c about 94 K. The superconducting transition temperature as a function of pressure, $T_c(P)$, was measured to 4.5 GPa. T_c was determined from ac susceptibility measurements and pressure was determined near T_c from shifts in ruby fluorescence peaks. T_c increases monotonically with $dT_c(P)/dP \approx 1.8$ K/GPa at ambient pressure. The volume as a function of pressure, $V(P)$, was measured to 10 GPa. The lattice parameters were determined by energy-dispersive x-ray-diffraction methods and pressure was determined from shifts in ruby fluorescence peaks. The volume decreases monotonically producing an isothermal bulk modulus $B_V = 104 \pm 17$ GPa at ambient pressure. Both results were combined to produce $T_c(V)$, which is more readily compared to theoretical models.

I. INTRODUCTION

Recently, the compound $HgBa_2CuO_{4+\delta}$ was found to be superconducting with T_c about 94 K.[1] This is a remarkably high value of T_c for a single CuO_2 layer per unit cell. For example, $TlBa_2CuO_{5-\delta}$ has a similar structure as $HgBa_2CuO_{4+\delta}$, but its T_c is less than 10 K.[2] It was surmised[1] and found[3] that the irreversibility field $H^*(T)$ is significantly higher for $HgBa_2CuO_{4+\delta}$ than for the two- and three-copper-layer Bi-Sr-Ca-Cu-O compounds, suggesting what is likely to be a significant improvement in technological applications.

Knowing the superconducting transition temperature as a function of pressure, $T_c(P)$, is important because that information can guide research directed at improving $T_c(0)$. In 1987, Chu *et al.* found that $(La_{0.9}Ba_{0.1})_2CuO_{4-y}$ with $T_c = 39$ K at ambient pressure increases to 52.5 K at 1.2 GPa, a rate of 11 K/GPa.[4] That led Chu *et al.* to discover $YBa_2Cu_3O_7$ with T_c above 90 K.[5] Recently, Chu *et al.* reported that T_c at 135 K for $HgBa_2Ca_2Cu_3O_{8+\delta}$ increases monotonically above 150 K at 15 GPa.[6] This opens the possibility to find a superconducting material with T_c above 150 K at ambient pressure. It is noteworthy that this temperature can be achieved by using ordinary household air-conditioning technology. Additionally, $T_c(P)$ measurements help in understanding the mechanism of superconductivity for new materials. In conjunction with the knowledge of the effect of pressure on volume, $V(P)$, $T_c(P)$ is transformed into $T_c(V)$, which can be directly compared with theoretical models.[7,8]

The samples of polycrystalline $HgBa_2CuO_{4+\delta}$ were grown. The growth procedures are detailed elsewhere.[3] The sample condition depended sensitively on the growth condition. One sample which was heated to 800 °C and annealed with oxygen at 200 °C for 2 h began to decompose in a week or two when it was exposed to the atmosphere, whereas another which was heated to 840 °C and annealed at 200 °C for 6 h did not. In both cases, the samples were kept in a dry box to reduce exposure to moisture. For this reason, samples which were annealed 6 h with O_2 were used for our measurements. Figure 1 shows the resistance as a function of temperature, $R(T)$. From room temperature to the transition temperature, R drops by a factor of about 4 demonstrating metallic behavior. The onset temperature is about 95 K and zero resitance is achieved at about 90 K. The onset temperature determined by resistance is slightly higher than that by the ac susceptibility, since the shielding effect takes place when the resistance reaches zero.

The magnetic susceptibility using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) was measured. Figure 2 shows the magnetic moment per mass, $\chi_m(T)$, in steps of 5 K. In an external field $H = 17$ Oe, the zero-field-cooling (ZFC) susceptibility amounts to -0.01 cm^3/g near 4 K.

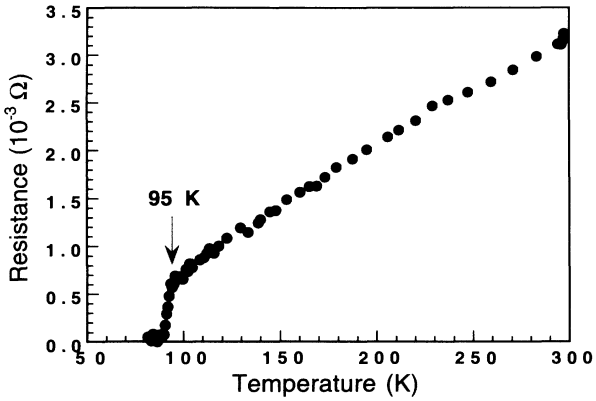

FIG. 1. Resistance for $HgBa_2CuO_{4+\delta}$ at ambient pressure.

The sample density is 7 g/cm^3 according to the crystal structure. The substitution of -0.01 cm^3/g into the equation $\chi_v(T) = \rho\chi_m(T)$ where $\rho = 7$ g/cm^3 yields -0.07, which is about 90% of $-1/4\pi$. So nearly 90% of the magnetic field is screened near 4 K. In the ZFC curve, additional features are seen at 75 K. This temperature is close to the onset temperature of the sintered sample before annealed in O_2.[3] The onset temperature is 90 K. The field-cooling (FC) susceptibility reaches ~20% of the maximum value of the ZFC susceptibility. This value represents a lower-bound value for the true superconducting volume fraction in the sample, indicating the bulk nature of superconductivity. The FC susceptibility reaches ~100% of its full low-temperature value within 5 K from onset T_c, consistent with the existence of a well defined phase.

Klehe et al. measured $T_c(P)$ for $HgBa_2CuO_{4+\delta}$ to 1 GPa using a helium-gas cell.[9] $T_c(P)$ for pressures higher than 1 GPa has not been reported yet. We report $T_c(P)$ to 4.5 GPa using a diamond anvil cell. Cornelius and Schilling[10] calculated the bulk modulus for $HgBa_2CuO_{4+\delta}$ to be 88 GPa. Their model for the calculation is developed from an empirical expression for the volume compressibility of the polyhedra.[11] We are not aware of any experimental measurements of $V(P)$ for $HgBa_2CuO_{4+\delta}$, from which the bulk modulus can be deduced. We report $V(P)$ to 10 GPa. Using this result, our $T_c(P)$ data are transformed into $T_c(V)$, which is compared with several theoretical predictions.

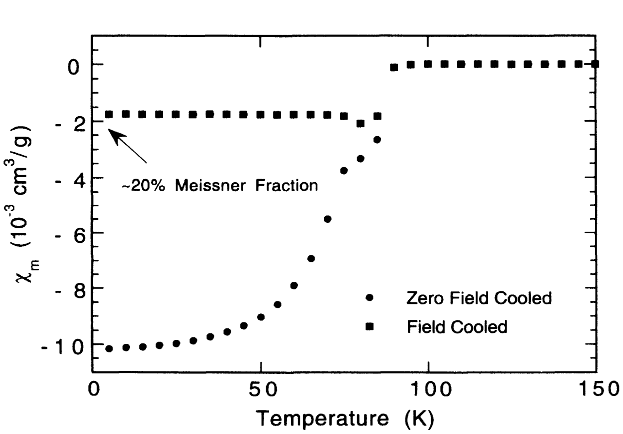

FIG. 2. Magnetic susceptibility for $HgBa_2CuO_{4+\delta}$ at ambient pressure.

II. PRESSURE DEPENDENCE ON T_c

Our system for $T_c(P)$ measurement has been described elsewhere[12–14] and has been improved to achieve better sensitivity and accuracy.[15] In this system, pressure is applied to the sample by the diamond anvil cell[16,17] (DAC) at room temperature, but is determined near T_c by measuring the R_1 and R_2 fluorescence peaks from ruby chips inside the pressure cavity. The importance of *in situ* pressure measurement has been demonstrated.[14,15] Silicone oil was used as the pressure medium. It was found that the customary high-pressure fluid, methanol:ethanol::4:1, destroys the superconducting properties of our polycrystalline samples of $HgBa_2CuO_{4+\delta}$. It is likely that H_2O in the mixture reacts with the sample and causes decomposition.[18] In contrast, the silicone oil does not affect the superconducting properties. It also remains transparent near T_c, thus allowing ruby fluorescence measurements.

T_c is obtained from the measurements of ac susceptibility, $\chi(T) = \chi'(T) + i\chi''(T)$.[19] The sample is located in one of the compensating coils. $\chi(T)$ is proportional to the voltage amplitude, $V(T) = V'(T) + iV''(T)$ of the compensating coils. The relatively small filling factor, although improved,[15] reduces the fraction of $V'(T)$ due to the sample superconductivity, $V'_{sc}(T)$. Thus, $V'_{sc}(T)$ is extracted from $V'(T)$ by subtracting the background, from which T_c is systematically determined.[15]

Two pieces of the sample were chosen to determine $T_c(P)$. The size of each piece was about $0.5 \times 0.5 \times 0.4$ mm^3 which ensures hydrostatic pressure inside pressure cavity whose diameter and thickness are 0.7 and 0.5 mm, respectively. One piece, sample A, has $T_c = 88.97 \pm 0.16$ K and the other, sample B, has $T_c = 90.96 \pm 0.05$ K at ambient pressure. The uncertainties were determined by considering only the statistical errors. The slight difference is reflective of the sample inhomogeneity. It may be due to the slight variation of oxygen content, δ, from region to region. Figure 3 shows $V'_{sc}(T)$ on increasing temperature at different pressures. For clarity, only the data obtained at selected pressures of 0.0, 1.9, 3.2, and 4.3 GPa for sample B are shown in this figure. The solid lines show the fit to the data to determine systematically T_c at onset temperature.[15] The transition width increases as pressure increases. This does not imply strong nonhydrostatic pressure, since the line width of the ruby fluorescence peaks did not show any sign of anomalous line broadening which arises from the uniaxial pressure, but may indicate the sample inhomogeneity or fragmentation. Due to the increase in the transition width, determination of $T_c(P)$ depends on the points chosen for T_c. Goldfarb et al.[19] discuss the disadvantage of using the midpoint. The width is also needed and these are field dependent. So they recommend the onset temperature

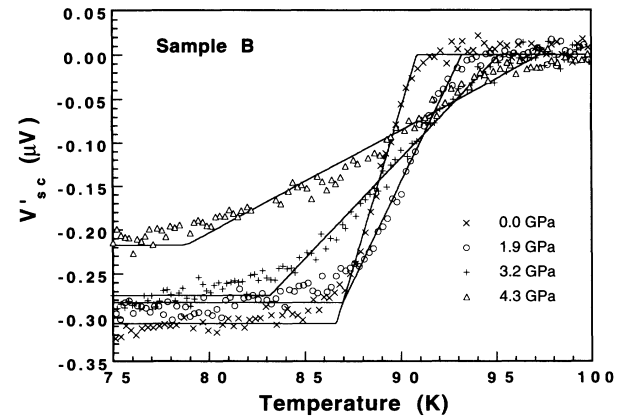

FIG. 3. $V'_{sc}(T)$ for sample B at selected pressures for clarity. The solid lines are fit to the data determining systematically T_c at onset temperature.

as the correct (closest to intrinsic) T_c. For these reasons, T_c is taken to be the onset temperature for the results of $T_c(P)$.

Figure 4 shows $T_c(P)$ for samples A and B. The errors for T_c as shown by the error bars in this figure were determined by taking only the statistical error into account during the fitting.[20] The errors generally increase as pressure increases where the signal-to-noise ratio is reduced. Up to 1 GPa, T_c increases at a rate of about 1.8 K/GPa. This value is close to the value reported by Klehe *et al.*[9] who reported $T_c(P)$ to 1 GPa using the He-gas cell. Above 1 GPa, the rate slightly reduces and remains nearly constant to 4.5 GPa. Our data do not indicate any sign of decrease or turnover up to 4.5 GPa and a linear fit appears reasonable. The solid lines are the fits by the straight line fixing $T_c(0)$ as given by the data. Sample A yields

$$T_c(P) = 88.97 + 1.45P \tag{1}$$

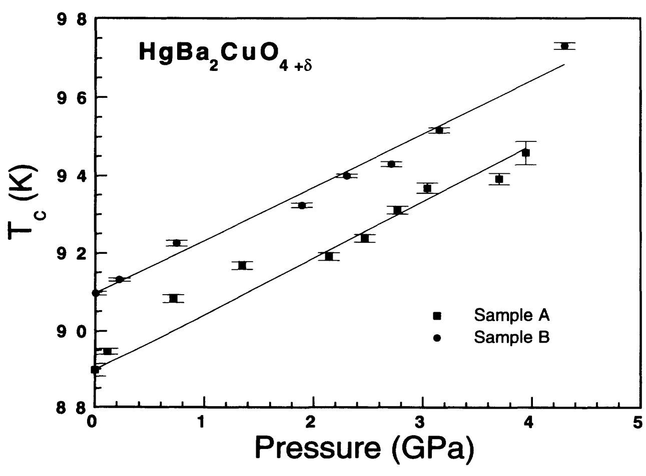

FIG. 4. $T_c(P)$ for both sample A and B to 4.5 GPa. The solid lines are the linear fit to the data.

with the fractional error 2.8% and sample B yields

$$T_c(P) = 90.96 + 1.37P \tag{2}$$

with the fractional error 0.9%. If the initial slope $dT_c(0)/dP$ is determined by these equations, $dT_c(0)/dP \approx 1.4$ K/GPa.

These initial slopes for $HgBa_2CuO_{4+\delta}$ are larger than those of superconducting $RBa_2Cu_3O_{7-\delta}$,[21] where R refers to rare earth atoms with $\delta \approx 0$, except $NdBa_2Cu_3O_{7-\delta}$.[14] In the case of $YBa_2Cu_3O_{7-\delta}$, the higher the initial slope, the lower $T_c(0)$.[22] Thus, the high initial slope implies that the optimum value of δ has not been achieved as demonstrated by increasing T_c on decreasing δ. If this trend is applicable to $HgBa_2CuO_{4+\delta}$, the high initial slope for $HgBa_2CuO_{4+\delta}$ indicates that $T_c(0)$ may increase further as δ changes to optimal value. At this moment, the values of δ for our samples are unknown. Work is in progress to determine $T_c(\delta)$.

Our measurements reveal that $T_c(P)$ for $HgBa_2CuO_{4+\delta}$ increases monotonically without showing any sign of decrease to 4.5 GPa. The homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n = 2$ and 3 have shown that T_c increases monotonically to 18 GPa without showing any sign of decrease.[6,23] A similar trend for $HgBa_2Ca_2Cu_3O_{8+\delta}$ to 23.5 GPa was observed by Nuñez-Regueiro *et al.*[24] At this moment, we do not know whether $T_c(P)$ for $HgBa_2CuO_{4+\delta}$ will follow that of the homologous series with $n = 2$ and 3 to 20 GPa. If so, $T_c(P)$ for this series appears to be different from that for other high-T_c superconducting materials such as $RBa_2Cu_3O_7$,[21] $Tl_2Ba_2CaCu_2O_{8+\delta}$,[12] $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$,[13] which show a change of sign in $dT_c(P)/dP$ at a pressure determined by the initial doping.

Wijingaarden *et al.* showed that $T_c(P)$ for $YBa_2Cu_4O_8$ shows the maximum at about 10 GPa, whereas that for $CaLaBaCu_4O_8$ increases monotonically to 50 GPa.[25] In both materials the carrier concentration on the Cu-O plane, $\delta_{\text{Cu-O}}$, increases monotonically as pressure increases. The only difference is that $d\delta_{\text{Cu-O}}(P)/dP$ for $YBa_{2-x}Cu_4O_8$ is greater than that for $CaLaBaCu_4O_8$. $T_c(P)$ for the homologous $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ is similar to that for $CaLaBaCu_4O_8$ in that $dT_c(P)/dP$ does not show the change of sign. Maybe $\delta_{\text{Cu-O}}$ for $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ increases more slowly, or possibly saturates to the optimal value at higher pressures. If the carrier concentration steadily increases on increasing P as shown in other high-T_c materials, T_c for these series may be insensitive to the change of carrier concentration at high pressures.

We want to be, however, cautious to draw such a conclusion. In case of $YBa_2Cu_3O_7$, Chu *et al.* observed from $R(T)$ that T_c monotonically increases to 16 GPa.[26] The pressure was measured with a Pb manometer. Later, Klotz *et al.*[27] found from $\chi(T)$ that T_c for $YBa_2Cu_3O_7$ has maximum at ~4 GPa in contrast to their measurements. The difference was ascribed to quasihydrostatic pressure by Chu *et al.*[26] This raises a slight doubt on $T_c(P)$ patterns for $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n = 2$ and 3 at higher pressures. It is worthwhile to determine $T_c(P)$ to very high pressure for $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$

with $n = 1$, 2, and 3 from $\chi(T)$ under hydrostatic conditions.

III. PRESSURE EFFECT ON VOLUME

We carried out energy dispersive x-ray-diffraction measurements[17] using the beam line X17C at the National Syncrotron Light Source. A Mao-Bell type DAC (Ref. 28) was used to obtain high pressures. The pressure medium for this study was same as for $T_c(P)$ measurements. The sample with this pressure medium did not show any anomalous change in the x-ray-diffraction patterns unlike the sample with methanol:ethanol::4:1. The pressure was measured in the same way as for $T_c(P)$ measurements.

The sample was ground into a fine powder and loaded into the pressure cavity whose diameter was about 0.3 mm. Each energy-dispersive diffraction spectrum was obtained with the detector fixed at $2\theta = 13.00°$. The measurement period for each spectrum was 10 min. Figure 5 shows a spectrum as taken at 1.10 GPa. Diffraction peaks from the sample are indexed accordingly. Those peaks which are not indexed are fluorescence peaks from the constituent atoms. A FORTRAN program is used to determine the peak position, intensity I, and linewidth Γ. All of the observed lines N from each spectrum are used to determine the lattice parameters by minimizing the weighted mean squared value[20]

$$\sigma^2 = \frac{1}{N}\sum_{j=1}^{N} w_j \left(\frac{1}{d^2_{\text{calc}}} - \frac{1}{d^2_{\text{obs}}}\right)^2 , \tag{3}$$

where $w_j \propto I/\Gamma$, $\sum_{j=1}^{N} w_j = N$, and d is the interatomic planar spacing. Considering the fractional error $\sigma_f = \sum |d^{-2}_{\text{calc}} - d^{-2}_{\text{obs}}| / \sum d^{-2}_{\text{obs}}$, all of the data could be fitted with σ_f varying from 1% to 6%.

Table I shows the resultant lattice parameters and volume at various pressures. We find $a = 3.8739(19)$ and $c = 9.5029(170)$ at ambient pressure and temperature. Putilin *et al.*[1] reported $a = 3.8797(5)$ and $c = 9.509(2)$ using x-ray powder data with a Rietveld refinement. Our a value is slightly smaller than theirs; our c value agrees. Chmaissem *et al.*[29] reported $a = 3.8829(6)$ and $c = 9.5129(14)$ for the sample containing 44% of $HgBa_2CuO_{4+\delta}$ using neutron powder diffraction data. Our a value is smaller than theirs; our c value agrees.

TABLE I. Values of lattice constants and volume for $HgBa_2CuO_{4+\delta}$ at various pressures. σ_f is as defined in the text.

P (GPa)	a (Å)	c (Å)	V (Å^3)	σ_f (%)
0.000	3.8739(19)	9.5029(0170)	142.61(0.39)	2
0.422	3.8690(11)	9.4627(0047)	141.65(0.15)	1
0.940	3.8700(13)	9.4917(0108)	142.16(0.26)	1
1.094	3.8584(36)	9.4332(0146)	140.44(0.48)	2
2.429	3.8430(57)	9.4286(0307)	139.25(0.87)	2
5.043	3.8364(97)	9.3725(1794)	137.94(3.35)	6
7.341	3.8143(42)	9.2960(0415)	135.24(0.91)	4
8.894	3.8079(53)	9.1888(0576)	133.24(1.21)	5

Figure 6 shows a/a_0, c/c_0, and V/V_0 as a function of pressure to 10 GPa. The lattice parameters as well as the volume decrease as pressure increases. Their values can be fitted to the Murnaghan equation of state.[30] We slightly extended it to

$$P = \frac{B_\alpha}{B'_\alpha}\left[\left(\frac{\alpha_0}{\alpha}\right)^{B'_\alpha} - 1\right], \tag{4}$$

where $\alpha = a$, c, or V, the subscript 0 indicates ambient pressure, $B_\alpha = \partial\alpha/\alpha\partial P$, and $B'_\alpha = \partial B_\alpha/\partial P$. We rearranged Eq. (4) as $\alpha(P)$ and fitted $\alpha(P)$. Table II shows the values of B_α and B'_α. The experimental value of $B_V = 104 \pm 17$ GPa is close to 88 GPa calculated by Cornelius and Schilling.[10] From their calculation, Cornelius and Schilling concluded that the material is most compressible among the known high-T_c superconductors. Our B_V value is larger than that of $RBa_2Cu_3O_7$ and La_2CuO_4, but similar or less than that of Bi-based superconductors.[21] On the other hand, the experimental

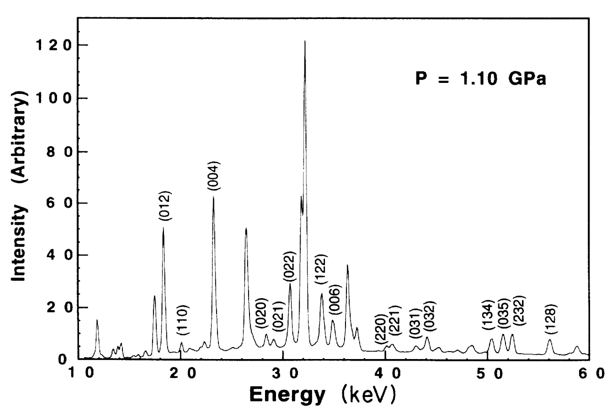

FIG. 5. Energy-dispersive x-ray diffraction for $HgBa_2CuO_{4+\delta}$ at 1.1 GPa.

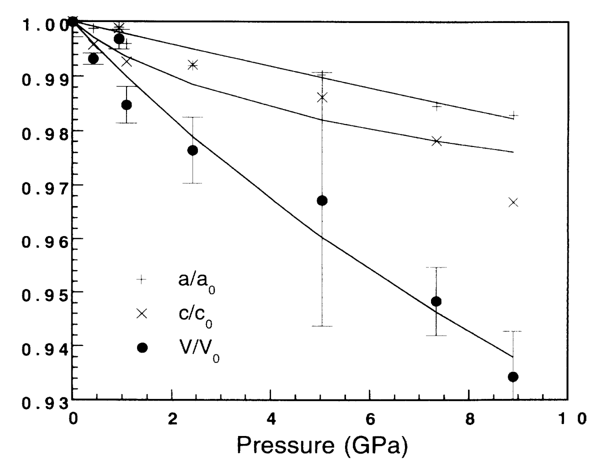

FIG. 6. a/a_0, c/c_0, and V/V_0 as a function of pressure to 10 GPa. For clarity, the error bars are drawn only for V/V_0.

TABLE II. Values of B_α and B'_α for $HgBa_2CuO_{4+\delta}$. Our experimental values are compared with some of the calculated values by Cornellius and Schilling (Ref. 10).

	B_a (GPa)	B'_a	B_c (GPa)	B'_c	B_V (GPa)	B'_V
This work	488±70	1.78	134±23	72.9	104±17	8.61
Ref. 12	250	-	294	-	88	-

value of $B_c = 1/\kappa_c$ for $HgBa_2CuO_{4+\delta}$ differs from the calculated value by about a factor of 3.[10] Our results reveal that the sample is 3 times more compressible along the c direction than along a or b direction. This feature is similar to that of $RBa_2Cu_3O_7$ (Ref. 21) and unlike La_2CuO_4 where $\kappa_a \approx \kappa_c$.

IV. T_c AS A FUNCTION OF VOLUME

$T_c(V)$ is more readily compared to theoretical model calculations than $T_c(P)$, because $T_c(V)$ relates T_c directly to the crystal structure. $T_c(V)$ can be obtained from our data using $T_c(P)$ and $V(P)$. We use Eq. (4) and values of B_V and B'_V in Table II to calculate V for a given value of P for sample B. $T_c(P)$ for one sample is chosen, since $T_c(P)$ for both samples has similar patterns. Figure 7 shows $T_c(V)$ obtained in this way. T_c monotonically increases as V decreases. There is no sign of saturation or turnover up to the smallest volume achieved in this experiment. The solid line is the fit with the equation

$$T_c = 233.34 - 0.9972V. \tag{5}$$

Several models for T_c were reviewed by Wijngaarden and Griessen.[7] In order to compare those models with the experimental values, they estimated

$$\frac{d\ln T_c}{d\ln V} = \frac{V}{T_c}\frac{dT_c}{dV} \tag{6}$$

at ambient pressure for various models and compared it with many experimental data. In our case, $T_c(V)$ is given as a set of numerical data, not as an analytical function. Instead of performing numerical differentiation, we adopted $dT_c/dV = -0.9972$ given in Eq. (5) to obtain $d\ln T_c/d\ln V$. This approach appears reasonable, since T_c is linearly proportional to V in this range. Figure 8 shows the results as a function of T_c. The magnitude of $d\ln T_c/d\ln V$ is in the order of -1.5, which is similar to that of other superconducting materials with $T_c \approx 90$ K. $d\ln T_c/d\ln V$ increases linearly as T_c increases.

The model based on BCS theory with electron-phonon interaction produces $d\ln T_c/d\ln V \approx -2$ which falls into the experimental value of superconducting materials with about $T_c = 90$ K at ambient pressure including this work. Wijngaarden and Griessen,[7] however, concluded that the model is not sufficient to explain $d\ln T_c/d\ln V$ of T_c at 40 K or 60 K at ambient pressure. On the other hand, BCS theory with pairing mechanism other than phonons fits into a number of systems covering the range from $T_c = 30$ K to 100 K at ambient pressure. We chose this model to compare with our data. Although their original intention was to compare $d\ln T_c/d\ln V$ at ambient pressure with experimental results with different system, we were interested in comparing this model with our data taken for the same system. The solid line in Fig. 8 represents the model reproduced from the equation

$$\frac{\partial \ln T_c}{\partial \ln V} = \frac{\partial \ln \Delta E}{\partial \ln V} + \frac{\partial \lambda}{\partial \ln V}\left[1 + \ln\left(\frac{k_B T_c}{\Delta E}\right)^2\right], \tag{7}$$

where the values of the parameters are the same as given, except changing $\Delta E/k_B$ from 500 K to 450 K.[7] This variation was necessary to change the magnitude of $d\ln T_c/d\ln V$ from about -3.5 to about -1.5 for comparison with our data. Apparently, the slope of our data is different from that of the model.

At this moment, we are not able to compare our experimental results of $T_c(V)$ with other theoretical models, because we do not know the exact values of the parameters in those models. Another important measurement will be the determination of atomic positions as a func-

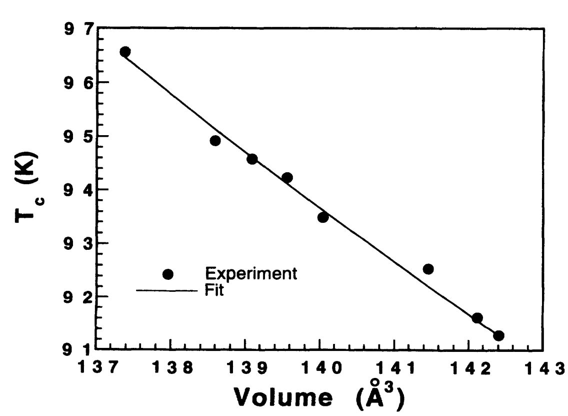

FIG. 7. $T_c(V)$ for sample B. The solid line is a linear fit to the data.

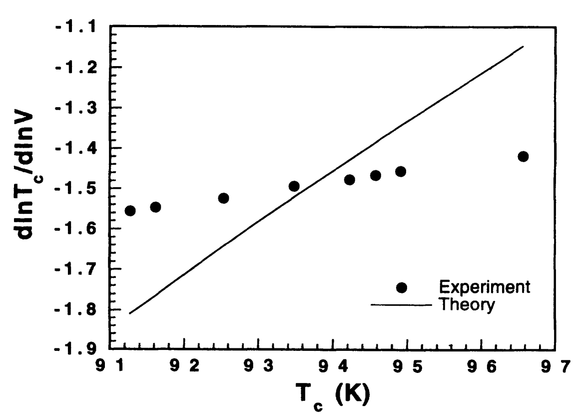

FIG. 8. $d\ln T_c/d\ln V$ as a function of T_c. The solid line is the calculated value based on BCS theory with pairing mechanism other than phonons.

tion of pressure. Because the material is layered, it is unknown whether the interlayer compressibility is proportional to κ_c. We plan such measurements in the near future. These measurements will also tell us the change of carrier concentration on the Cu-O plane as a function of volume.

V. CONCLUSION

We have found $T_c(P)$ for $HgBa_2CuO_{4+\delta}$ to 4.5 GPa. Unlike other superconducting materials with T_c about 90 K or above, T_c increases monotonically without any sign of decrease as P increases. We conjecture that T_c may increase continually on increasing P, as observed in the homogolous system $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n =$ 2 and 3. This system, therefore, indicates that T_c can be further improved either by proper chemical substitution, or by optimal oxygen doping. We have also determined $V(P)$, from which $B_V = 104 \pm 17$ GPa was obtained. The experimental value of B_V is close to the calculated value of 88 GPa by Cornelius and Schilling.[10] Unlike their calculated result of $\kappa_a \approx \kappa_c$, our experimental results show that κ_c is greater than κ_a by a factor of 3.

We have produced $T_c(V)$ for $HgBa_2CuO_{4+\delta}$ from the measured values of $T_c(P)$ and $V(P)$. For comparison with other models, $d\ln T_c/d\ln V$ also has been generated. $d\ln T_c/d\ln V$ is about -1.5 like other high-T_c superconducting materials with T_c about or above 90 K. The results were compared with the model based on the BCS-like theory with pairing mechanism other than phonon-electron interaction. This model is unable to describe the experimental result even with variation of one input parameter. It may be, however, too early to make such a conclusion and we await more detailed calculations. Many other models have been suggested in the past. We expect that our experimental results will help in refining those models.

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