

Volume dependence of the superconducting transition temperature for the high-temperature superconductor $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$

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The homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1, 2, 3, 4$) is 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. We slightly doped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with Pb, producing $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ with T_c about 133 K. The Pb dopant helped material growth and still kept T_c close to that of the optimally doped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$. The superconducting transition temperature as a function of pressure, $T_c(P)$, was measured to 3 GPa. T_c increases monotonically with $dT_c(P)/dP \approx 1.5$ K/GPa near ambient pressure. The lattice parameters as a function of pressure were measured to 5 GPa. The volume decreases monotonically and is represented by an isothermal bulk modulus of $B_V = 143 \pm 15$ GPa. Both results were combined to produce $T_c(V)$, which is readily comparable to theoretical models.

I. INTRODUCTION

The homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1, 2, 3, 4$) is the newest and most promising of the layered high- T_c superconducting materials with values of the transition temperature $T_c \approx 94$ K,¹ 127 K,² 134 K,³ and 126 K,⁴ respectively. It was found⁵ that the irreversibility field $H^*(T)$ is significantly higher for $\text{HgBa}_2\text{CuO}_{4+\delta}$ 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. $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (Hg1223) contains three Cu-O planes per unit cell and sets the highest $T_c = 134$ K among the known high-temperature superconductors.

Knowing the superconducting transition temperature as a function of pressure, $T_c(P)$, is important because that information can guide research directed at improving $T_c(0)$.^{6,7} Several works have been reported on $T_c(P)$ for Hg1223. Chu *et al.* reported that T_c at 135 K for Hg1223 increases monotonically above 150 K at 15 GPa.⁸ Gao *et al.* reported that T_c for Hg1223 increased as high as 164 K under 30 GPa.⁹ Ihara *et al.* found that T_c for Hg1223 has the maximum value of 156 K at 25 GPa.¹⁰ These results open the possibility of finding a new material with T_c higher than 150 K, a temperature that can be maintained by conventional freon cooling technology.

According to these experiments,⁸⁻¹⁰ T_c for Hg1223 varies at a rate of 1.0 K/GPa or less up to about 20 GPa. Those results, however, do not allow precise determination of $dT_c(P)/dP$ in the low pressure range. Moreover, those experiments were performed under quasihy-

drostatic pressure conditions and pressure was not measured near T_c . Recently, Klehe *et al.* measured T_c to 0.9 GPa using a He-gas cell which ensured hydrostatic pressure and measured the pressure near T_c .¹¹ They found that Hg1223 has $dT_c(P)/dP = 1.75$ K/GPa, which is similar to that of $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg1201) (Ref. 12) and $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg1212).¹¹

We have prepared $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ (HgPb1223), T_c of which is about 133 K close to that of Hg1223. $T_c(P)$ for HgPb1223 has not been reported yet. $T_c(P)$ measurement in conjunction with $V(P)$ leads to $T_c(V)$, which helps in understanding the mechanism of superconductivity for new materials. We measured $T_c(P)$ to 3 GPa and the lattice parameters to 5 GPa. We have found that the pressure derivative slightly decreases as pressure increases. For example, our value of $dT_c(P)/dP$ for HgPb1223 is about 1.7 K/GPa to 1 GPa close to that for Hg1223 reported by Klehe *et al.*¹¹ and about 1.14 ± 0.03 K/GPa to 3 GPa. The volume decreases monotonically producing an isothermal bulk modulus $B_V = 143 \pm 15$ GPa, which is larger than the value of 93 GPa for Hg1223 reported by Hunter *et al.*¹³ Combining our measured values of $V(P)$ and $T_c(P)$ leads to $T_c(V)$, which can be readily compared with theoretical models.^{14,15} Specifically, the logarithmic volume derivative $d \ln T_c / d \ln V$ is presented as a function of V/V_0 where V_0 is a volume at ambient pressure and is compared with those models.

II. SAMPLE PROPERTIES

HgPb1223 was grown by the usual solid state reaction technique. The growth procedures are detailed

elsewhere.¹⁶ Among various materials made by the low pressure technique, several pieces of material from the same batch are used for this study. Figure 1 shows the resistance as a function of temperature, $R(T)$. From room temperature to the superconducting transition temperature, R drops by a factor of about 2 demonstrating the metallic property. The onset temperature is about 133 K and the resistance reaches zero near 130 K. The onset temperature determined by resistance is slightly higher than that by the ac susceptibility due to the shielding effect that takes place when the resistance reaches zero.

The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design). Figure 2 shows the magnetic moment per unit mass, $\chi_m(T)$. The sharp transition occurring around 130 K confirms superconductivity. In an external field $H = 15$ Oe, the zero field cooling (ZFC) susceptibility amounts to $-0.016 \text{ cm}^3/\text{g}$ near 4 K. The x-ray density is $\rho = 6.2 \text{ g/cm}^3$ according to the lattice parameters determined from our x-ray diffraction measurement. The actual density based on the measured size and mass is about 4.5 g/cm^3 which is 73% of the x-ray density. Klehe *et al.*¹¹ reported that the actual density for the polycrystalline Hg1223 was 60% of the x-ray density. If ρ is assumed to be 4.5 g/cm^3 the equation $\chi_v(T) = \rho\chi_m(T)$ yields -0.072 . Based on this result, nearly 90% of the magnetic field is screened near 4 K. In the ZFC curve, the additional feature is seen around 90 K. After the sample was ground it disappeared indicating that it is largely due to the intergranular transition.¹⁶ The field-cooling (FC) susceptibility reaches $\sim 20\%$ of the maximum value of 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 $\sim 100\%$ of its full low-temperature value within 20 K from onset T_c .

The x-ray diffraction patterns were obtained and the Rietveld refinement was performed using the General Structure Analysis System by Larson *et al.*¹⁷ The detailed results are reported elsewhere.¹⁶ The results lead to $a = 3.8499(2) \text{ \AA}$ and $c = 15.8491(18) \text{ \AA}$. Chmaissem *et al.* reported $a = 3.8502(1) \text{ \AA}$ and $c = 15.7829(9) \text{ \AA}$

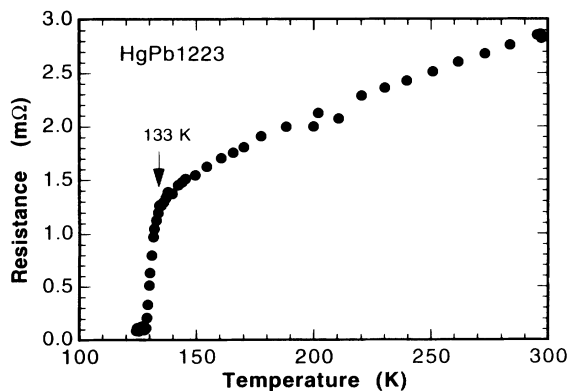


FIG. 1. Resistance for the polycrystalline $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ at ambient pressure.

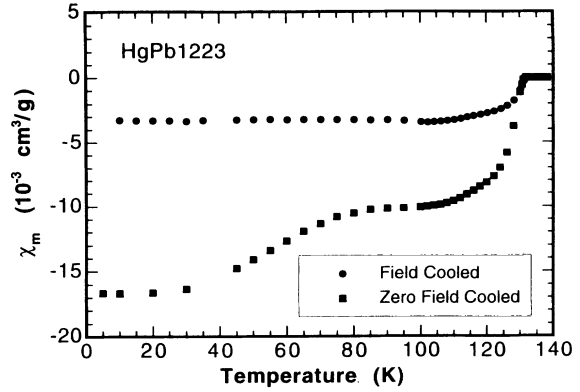


FIG. 2. Magnetic susceptibility for the polycrystalline $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ at ambient pressure.

\AA from the neutron powder diffraction data for Hg1223.¹⁸ Our c value is slightly larger than theirs. This may be due to the Pb atom present in our sample. The stoichiometry of Hg:Pb:Ba:Ca:Cu:O before reaction was 0.8:0.2:2:1.75:3:7.75. The composition of the grown sample was measured by energy dispersive x-ray spectroscopy (EDX). The composition ratios of Hg:Pb:Ba:Ca:Cu turned out to be 1.16(3):0.14(1):2.00:1.38(4):2.56(8) where the results were normalized with respect to two Ba atoms. It is commonly assumed that Pb substitutes on the Hg site.^{19–21} According to EDX results it is unlikely that Pb partially occupies the Hg site. So, the Rietveld refinement was performed assuming that Pb could occupy any one of Hg, Ba, or Ca sites. R_p was lowest when Pb partially occupied the Ca site leading to $\text{HgBa}_2\text{Cu}_{2.86}\text{Ca}_{1.73}\text{Pb}_{0.17}\text{O}_{8+\delta}$.

The x-ray diffraction data reveal that the sample contains impurities and other defects. On the other hand, the $R(T)$ and $\chi_m(T)$ data indicate that the majority of the material contains a single superconducting phase. The role of Pb, however, remains unknown. Pb is initially introduced to help in growing Hg1223. The substitution of Pb into Hg1223 did not appear to affect the superconducting properties of Hg1223, since T_c remains same as that of Hg1223. $\chi_m(T)$ for HgPb1223 is even better than those for Hg1223 by other groups^{3,18} in that the superconducting transition around 130 K is more clearly defined. In light of x-ray diffraction and EDX results, we imagine that Pb substitutes into the Ca site every other 10 unit cells. This may have been necessary to stabilize the atomic structure of Hg1223. The bulk modulus as a function of Pb composition may be able to answer this question. Additional studies of this phenomena between the structural stability and Pb doping are in progress.

III. PRESSURE DEPENDENCE ON T_c

Our system for $T_c(P)$ measurement has been described elsewhere.^{22,23} In this system, pressure is applied to the sample by the diamond anvil cell^{24,25} (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.^{22,23} Silicone oil was used as the pressure medium. The size of the sample was about $0.5 \times 0.5 \times 0.4$ mm which ensures hydrostatic pressure inside the cylindrical pressure cavity whose diameter and thickness are 0.7 and 0.5 mm, respectively.

T_c is determined from the ac susceptibility, $\chi(T) = \chi'(T) + i\chi''(T)$.²⁶ $\chi(T)$ is proportional to the voltage amplitude, $V(T) = V'(T) + iV''(T)$, of the compensating coils where the sample is located. So, $V(T)$ is measured on increasing temperature at a rate of 0.6 K/min and on decreasing temperature at a rate of 2.5 K/min. The relatively small filling factor, although improved,²² has a poor 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.²² Figure 3 shows $V_{sc}(T) = V'_{sc}(T) + iV''_{sc}(T)$ on increasing temperature. The negative and positive values of the voltage correspond to $V'_{sc}(T)$ and $V''_{sc}(T)$, respectively. For clarity, only the data obtained at selected pressures of 0.00, 1.37, and 3.10 GPa are shown. $V'_{sc}(T)$ shows the superconducting transition due to the intrinsic diamagnetic shielding above 130 K; its counterpart in $V''_{sc}(T)$ is too weak to be shown.²⁷ The peaks in $V''_{sc}(T)$ around 120 K are due to the coupling diamagnetic shielding between the grains. The peak height decreases and eventually dies away as pressure increases. The contacts between the grains probably improves at higher pressure and reduces the coupling loss. The information from $V''_{sc}(T)$, however, is not sufficient to quantify due to other effects under pressure.

The transition width increases as pressure increases. This does not necessarily imply strong nonhydrostatic pressure, since the linewidth of the ruby fluorescence peaks did not show any sign of anomalous broadening, usually associated with uniaxial pressure, rather this may indicate the sample inhomogeneity or fragmentation. Due to the increase in the transition width, deter-

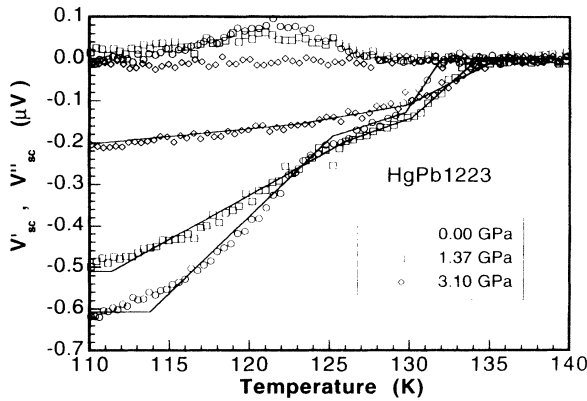


FIG. 3. $V_{sc}(T) = V'_{sc}(T) + iV''_{sc}(T)$ for the polycrystalline $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ at selected pressures for clarity. The data are also presented every other four points for clarity. The solid lines are fit to the data of $V'_{sc}(T)$ determining systematically T_c at onset temperature.

mination of $T_c(P)$ depends on the points chosen for T_c . Goldfarb *et al.*²⁶ discussed the disadvantage of using the midpoint. The width is also needed and these are field dependent, so they recommended the 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 $T_c(P)$. In order to determine T_c systematically $V'_{sc}(T)$ can be usually fitted by two flat and one straight line.²² Due to a large hump below T_c the accurate determination of onset temperature was plausible when the data were fitted by the two flat and three straight lines,

$$f(T; h_j, t_j) = \begin{cases} h_1 & \text{for } T < t_1 \\ a_1 + b_1 T & \text{for } t_1 \leq T < t_2 \\ a_2 + b_2 T & \text{for } t_2 \leq T < t_3 \\ a_3 + b_3 T & \text{for } t_3 \leq T < t_4 \\ h_4 & \text{for } t_4 \leq T \end{cases} \quad (1)$$

where $b_j = (h_{j+1} - h_j)/(t_{j+1} - t_j)$, $a_j = h_j - b_j t_j$, and $j = 1, 2, 3$. From this fit, t_4 is chosen to represent T_c for this study.

The solid squares in Fig. 4 show $T_c(P)$ for HgPb_{1223} . T_c for HgPb_{1223} at ambient pressure is 131.7 ± 0.2 K. The errors for T_c are on the order of 0.2 K based on the statistical error associated with the fitting²⁸ and are not shown in this figure. The errors slightly increase as pressure increases due to the reduced signal-to-noise ratio. Between the first at ambient pressure and the next point, T_c increases at a rate of 1.5 K/GPa, which is slightly less than 1.75 K/GPa for the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ as reported by Klehe *et al.*¹¹ The small difference may be due to the presence of the Pb atom. As pressure increases above 1 GPa, the rate slightly reduces. The slight change in the rate is understood in light of $V(P)$ which also indicates the slower rate above 1 GPa (see Sec. IV). Above 2 GPa the rate remains nearly constant. The solid line is the linear fit fixing $T_c(0)$ as given by the data. The fit yields $dT_c(P)/dP = 1.14 \pm 0.03$ K/GPa. This result is reproducible in that pressure effect on another sample yields the same pressure derivative. Notice that the pressure derivative depends on the pressure range. Clearly, cau-

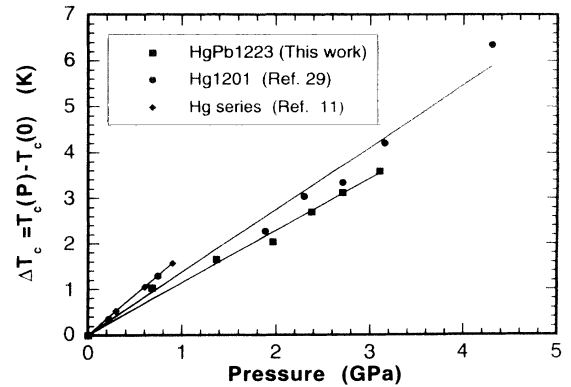


FIG. 4. Comparison of $T_c(P)$ for the polycrystalline $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ with others. The solid lines are the linear fit to the data.

tion must be exercised in referring to the pressure derivative.

Figure 4 also compares the current result with others. $T_c(P)$ for Hg1201 in an earlier paper²⁹ is shown by the solid circles. The pressure derivative to 4.5 GPa was found to be 1.40 ± 0.03 K/GPa. Klehe *et al.* found that all of the pressure derivatives of Hg1201, Hg1212, and Hg1223 to 1 GPa are close to 1.75 K/GPa. Their results are reproduced by the solid diamonds in steps of 0.3 GPa. The pressure derivative between the point at ambient pressure and the next point of our results for Hg1201 is essentially the same as theirs. In light of their results, we also expect that the pressure derivatives of Hg1212 and Hg1223 may be similar to the pressure derivative of Hg1201 to higher pressure. $dT_c(P)/dP$ for HgPb1223, however, is 1.14 ± 0.03 K/GPa up to 3 GPa which is slightly less than that for Hg1201. Work is in progress to see the effect of the Pb composition on the pressure derivative. The initial slope for HgPb1223 is still larger than those of superconducting $RBa_2Cu_3O_{7-\delta}$,³⁰ where R refers to rare earth atoms with $\delta \approx 0$, except $NdBa_2Cu_3O_{7-\delta}$.²³

It has been found that T_c for Hg1201, Hg1212, and Hg1223 increases monotonically to 4.5 GPa,²⁹ 18 GPa,⁸ and 18 GPa,³¹ respectively, without showing any sign of decrease. A similar trend for Hg1223 to 23.5 GPa was observed by Nuñez-Regueiro *et al.*³² Our result for HgPb1223 shows the similar trend to 3 GPa. On the other hand, Ihara *et al.* found that T_c for Hg1223 and the mixture of Hg1223 and Hg1234 have maxima at 13 GPa and 25 GPa, respectively.¹⁰ In any case, $T_c(P)$ for this series is different from that for other high- T_c superconducting materials such as $RBa_2Cu_3O_7$,³⁰ $Tl_2Ba_2CaCu_2O_{8+\delta}$,³³ and $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$,³⁴ which show a change of sign in $dT_c(P)/dP$ at pressures below 10 GPa. Wijngaarden *et al.* showed that $T_c(P)$ for $YBa_2Cu_4O_8$ has a maximum at about 10 GPa, whereas $T_c(P)$ for $CaLaBaCu_4O_8$ shows a monotonic increase to 50 GPa.³⁵ In both materials the carrier concentration on the Cu-O plane, δ_{CuO} , increases monotonically as pressure increases. The only difference is that $d\delta_{CuO}(P)/dP$ for $YBa_{2-x}Cu_4O_8$ is greater than that for $CaLaBaCu_4O_8$. Perhaps δ_{CuO} for $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ increases more slowly, or possibly saturates to an optimal value at higher pressures.

IV. PRESSURE EFFECT ON VOLUME

We carried out energy dispersive x-ray diffraction measurements²⁵ using the beam line X17C at the National Synchrotron Light Source. A Mao-Bell type DAC (Ref. 36) was used to obtain high pressures. The pressure medium for this study was the same as for $T_c(P)$ measurements. 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 a pressure cavity with a diameter of about 0.3 mm. Each energy dispersive diffraction spectra were obtained with an intrinsic Ge detector fixed at 2θ angle. The

diffraction angle, 2θ , was calibrated by the energy dispersive diffraction spectrum for gold powder, which led to $2\theta = 13.037^\circ$. The measurement period for each spectrum was 10 min. Figure 5 shows a spectrum taken at 5.13 GPa. Some peaks are from fluorescence of the constituent atoms excited by the incident x rays and others are due to the diffraction from the sample. The movements of the powder in the pressure cavity with changes in pressure cause the peak intensity to vary and in some cases caused it to disappear from one pressure to another. The seven peaks indexed in Fig. 5 appear consistently to the highest pressure and were used for the determination of lattice parameters. A spectrum analysis program was used to determine the peak position, intensity, I , and line width, Γ , for each spectrum. Based on these values the lattice parameters are determined by minimizing the weighted mean squared value,²⁸

$$\sigma^2 = \frac{1}{N} \sum_{j=1}^N w_j \left(\frac{1}{d_{cal}^2} - \frac{1}{d_{obs}^2} \right)^2, \quad (2)$$

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

Table I shows the resultant lattice parameters and volume at various pressures. We find $a = 3.8507(27)$ Å and $c = 15.8423(124)$ Å at ambient pressure and temperature. Considering the uncertainties these values are essentially the same as $a = 3.8499(2)$ Å and $c = 15.8491(18)$ Å obtained from the angular dispersive x-ray diffraction (see Sec. I). Figure 6 shows 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 . Their values can be fitted by the Murnaghan equation of state,³⁷ which is rearranged and extended to

$$\alpha = \alpha_0 \left(\frac{B'_\alpha}{B_\alpha} P + 1 \right)^{-\frac{1}{B'_\alpha}}, \quad (3)$$

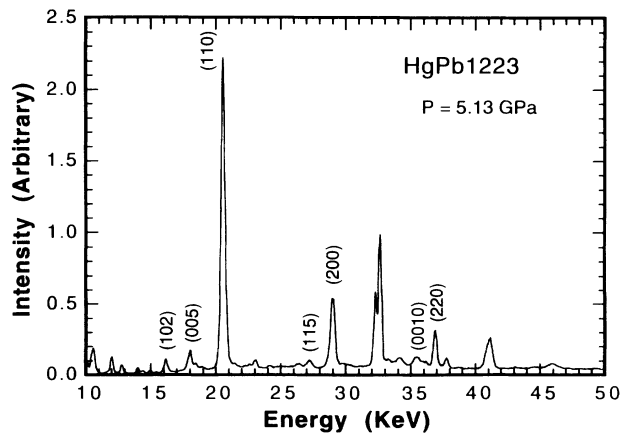


FIG. 5. Energy dispersive x-ray diffraction for the powdered $HgBa_2CuCa_{2-x}Pb_xO_{8+\delta}$ at 5.13 GPa.

TABLE I. Values of lattice constants and volume for $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ at various pressures. σ_f is as defined in the text.

P (GPa)	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	σ_f (%)
0.00	3.8507(27)	15.8423(124)	234.91(0.52)	4
1.03	3.8439(25)	15.7762(298)	233.11(0.74)	4
2.33	3.8406(42)	15.7237(305)	231.92(0.96)	5
3.00	3.8327(35)	15.6730(218)	230.23(0.75)	4
3.49	3.8263(32)	15.6666(556)	229.36(1.19)	4
5.13	3.8148(52)	15.5856(738)	226.81(1.70)	5

where $\alpha = a, c$, or V , the subscript 0 indicates ambient pressure, $B_\alpha = \partial\alpha/\partial P$, and $B'_\alpha = \partial B_\alpha/\partial P$. The solid lines in Fig. 6 show the resultant fit by Eq. (3).

Table II shows the corresponding values of B_α and B'_α . The number of data in Table I is not sufficient to determine B'_α unambiguously and so the value of B'_α is fixed during the fit as indicated by the question mark (?) in the table. Our result reveals that $\kappa_c/\kappa_a = B_a/B_c = 2.3$. According to our result, the material is more compressible along the c axis than the a axis. This feature is similar to that of $\text{RBa}_2\text{Cu}_3\text{O}_7$ and unlike La_2CuO_4 where $\kappa_a \approx \kappa_c$.³⁰ The compressibility of HgPb1223 has not been reported yet. Although the comparison of our results for HgPb1223 with others for Hg1223 may not be straightforward, the calculated results by Cornelius *et al.*³⁸ for Hg1223 are listed in Table II. The bulk modulus for HgPb1223 is $B_V = 143 \pm 17$ GPa. The bulk modulus for Hg1223 has been reported as 101 GPa,³⁸ 92.6 GPa,¹³ and 82.6 ± 10 GPa.³⁹ Assuming that B_V for Hg1223 is about 100 GPa, doping Hg1223 with Pb may have hardened Hg1223 . In light of this result, HgPb1223 is structurally more stable than Hg1223 .

We, however, want to be cautious in drawing such a conclusion since the experimental errors involved can prevent us from making such a direct comparison. We noticed the large discrepancy between our value of B_V and others. For example, our value of $B_V = 104$ GPa²⁹ for Hg1201 is larger than $B_V = 69.4$ GPa by Hunter *et al.*¹³ and $B_V = 65.4$ GPa by Eggert *et al.*³⁹ This kind of discrepancy has been shown in the literature with other materials.³⁰ To confirm whether HgPb1223 is harder than Hg1223 , work is in progress to determine B_V as a function of the Pb composition.

V. 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 di-

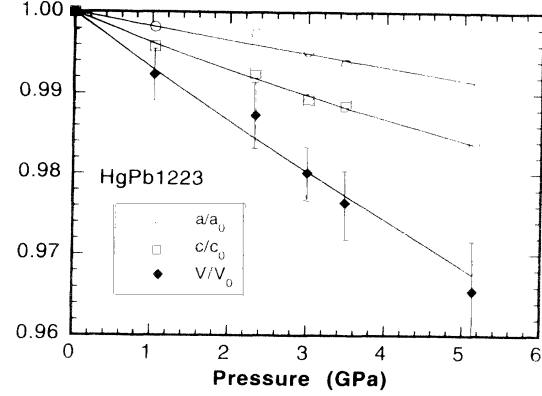


FIG. 6. a/a_0 , c/c_0 , and V/V_0 as a function of pressure to 5 GPa. For clarity, the error bars are drawn only for V/V_0 . The solid lines are the resultant fit by Eq. (3).

rectly to the crystal structure. $T_c(V)$ can be obtained from our data using $T_c(P)$ and $V(P)$. One method is to use Eq. (3) and values of B_V and B'_V in Table II. We have pointed out that a slight nonlinear variation is found around 2 GPa in the data for both $T_c(P)$ and $V(P)$. For this reason, we fitted the data of $V(P)$ with the fourth order polynomial, fixing the initial position at ambient pressure. The result is used to calculate V for a given value of P . The solid squares in Fig. 7 are generated in this way. For comparison, the results are shown as a function of V/V_0 . T_c monotonically increases with decreasing V/V_0 . There is no sign of saturation or turnover up to the smallest volume achieved in this experiment. The solid line is a linear fit fixing $T_c(V_0)$ as given. The fractional error is 0.3% indicating that T_c is very nearly linear to V .

The solid circles in Fig. 7 show $T_c(V/V_0)$ for Hg1201 .²² The normalized volume derivative, $dT_c(V/V_0)/d(V/V_0)$, for HgPb1223 and Hg1223 is -186.6 K and -161.6 K, respectively. As shown in Fig. 4, ΔT_c for HgPb1223 is always *lower* for a given amount of the pressure change than that for Hg1201 . On the other hand, ΔT_c for HgPb1223 is always *higher* for a given amount of the normalized volume change than that for Hg1201 . In view of this comparison we imagine that T_c for the three-layer system is more boosted for a given amount of change in the interlayer distance than that for a one-layer system assuming that the Cu-O interlayer compressibility is proportional to κ_c .

Several models for $T_c(V)$ were reviewed by Wijngaar-

TABLE II. Values of B_α and B'_α for $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$, where $\alpha = a, c$, or V . Our results are compared with the calculated values for Hg1223 by Cornelius *et al.* (Ref. 38) and experimental results for Hg1201 by Kim *et al.* (Ref. 29) A question mark (?) indicates that the uncertainty is unknown; a dash (-) indicates that the corresponding values are not available.

Material	B_a (GPa)	B'_a	B_c (GPa)	B'_c	B_V (GPa)	B'_V
HgPb1223 (this work)	586(49)	2(?)	255(113)	24(?)	143(15)	5(?)
Hg1223 (Ref. 38)	345(?)	-	250(?)	-	101(?)	-
Hg1201 (Ref. 29)	488(70)	2(?)	134(23)	73(?)	104(17)	9(?)

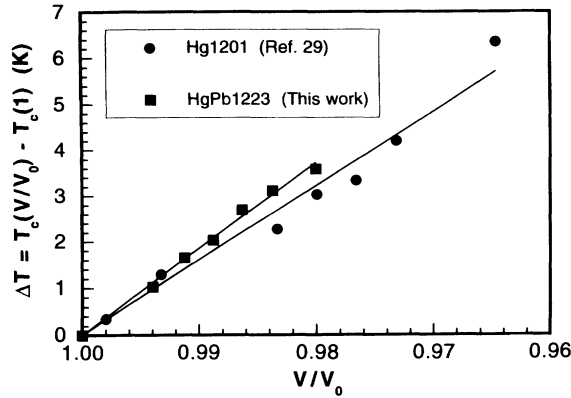


FIG. 7. Comparison of $T_c(V/V_0)$ for the polycrystalline $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ with others. The solid line is a linear fit to the data.

den *et al.*¹⁴ In order to compare those models with the experimental values, they estimated

$$\frac{d \ln T_c}{d \ln V} = \frac{V}{T_c} \frac{dT_c}{dV} \quad (4)$$

at ambient pressure and compared it with experimental data. Our results shown in Fig. 7 can be transformed into $d \ln T_c / d \ln V$. One way is to differentiate Eq. (4) with respect to V . Another way is to perform the numerical differentiation over the $T_c(V)$ data. Instead, we substitute $dT_c/dV = -0.7945$ into Eq. (4) and use the data for V and T_c to obtain $d \ln T_c / d \ln V$. This approach is a reasonable compromise between the pure analytical solution and pure numerical solution and does not require a direct use of the bulk modulus whose values differ from literature to literature. Figure 8 shows the results as a function of V/V_0 . $d \ln T_c / d \ln V$ for HgPb1223 is in the order of -1.4 and increases linearly as T_c increases. The results are compared with $d \ln T_c / d \ln V$ for Hg1201.²² The values for Hg1201 are lower than those for HgPb1223, but the slopes for these two different systems are equivalent within their combined uncertainty. Klehe *et al.* reported that all of $d \ln T_c / d \ln V$ for the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ near the ambient pressure have same value of -1.2 .¹¹ Our values are generally lower than theirs. Knowing that their values of T_c , V , and dT_c/dP are similar to ours, the discrepancy is mainly due to the difference in the bulk modulus.

Wijnngaarden *et al.*¹⁴ noticed that the model based on BCS theory with electron-phonon interaction produced $d \ln T_c / d \ln V \approx -2$ which falls into the experimental value of superconducting materials with T_c above 90 K. They, however, concluded that the model was 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 a 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 experi-

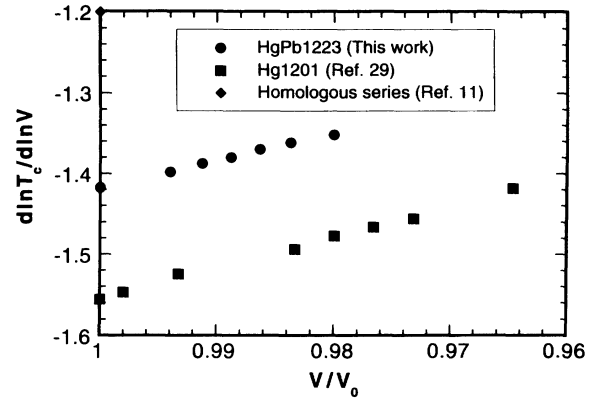


FIG. 8. $d \ln T_c / d \ln V$ as a function of V/V_0 . The results are compared.

mental results of different systems, we were interested in comparing this model with our data taken for the same system. The solid line in Fig. 9 is obtained from the model reproduced from the following equation:

$$\frac{\partial \ln T_c}{\partial \ln V} = \frac{\partial \ln \Delta E}{\partial \ln V} + \frac{\partial \lambda}{\partial \ln V} \left[1 + \ln \left(\frac{k_B T_c}{\Delta E} \right)^2 \right], \quad (5)$$

where $\partial \ln \Delta E / \partial \ln V = 2$ and $\partial \lambda / \partial \ln V = -10$ as given,¹⁴ except changing $\Delta E/k_B$ from 500 K to 650 K. This variation was necessary to change the magnitude of $d \ln T_c / d \ln V$ from about 1 to about -1.5 for comparison with our data. Still, the slope of our data is different from that of the model. In an attempt to compare our data of $d \ln T_c / d \ln V$ for Hg1201 with this model, we had to change $\Delta E/k_B$ from 500 K to 450 K.²² In light of this picture, the superconducting energy gap ΔE of HgPb1223 appears greater than that of Hg1201. One, however, has to be aware of the large approximation involved in this analysis.

At this moment, we are not able to compare our experimental results of $T_c(V)$ with other theoretical mod-

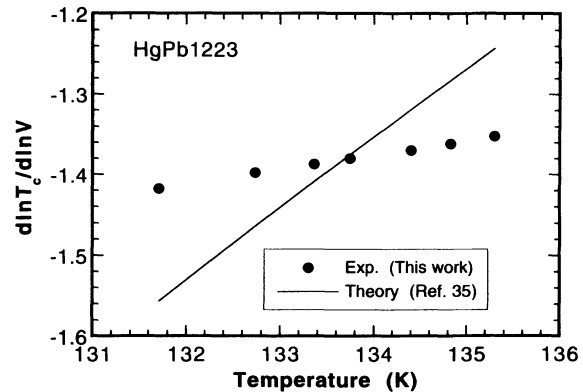


FIG. 9. $d \ln T_c / d \ln V$ for the polycrystalline $\text{HgBa}_2\text{CuCa}_{2-x}\text{Pb}_x\text{O}_{8+\delta}$ as a function of T_c . The solid line is the calculated value based on BCS theory with pairing mechanism other than phonons.

els, because we do not know the values of the parameters in those models. Another important measurement will be the determination of atomic positions as a function of pressure. Since the material is layered it is unknown whether the inter-layer compressibility is proportional to κ_c . We plan such measurements in the near future. These measurements will also tell us the change of $\delta_{\text{Cu-O}}$ plane as a function of volume. Consequently, T_c can be expressed as a function of $\delta_{\text{Cu-O}}$.

VI. CONCLUSION

We have synthesized HgPb1223. Despite a small amount of Pb added to Hg1223, T_c remains the same as that of Hg1223. The x-ray diffraction data reveal only a single phase with apparent impurities and defects. The resistance and dc susceptibility measurements indicate a well-defined superconducting phase around 133 K. We have measured $T_c(P)$ for HgPb1223 to 3 GPa. In the lower pressure range below 1 GPa, dT_c/dP is 1.5 K/GPa slightly less than 1.75 K/GPa for the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ as established by Klehe *et al.*¹¹ Assuming T_c is linear in P , dT_c/dP for HgPb1223 is found to be 1.14 ± 0.03 K/GPa to 3 GPa, which is slightly lower than 1.40 ± 0.03 K/GPa for Hg1201 to 4.5 GPa.²² We wish to determine T_c as well as dT_c/dP as a function of the Pb composition.

We have determined $a(P)$, $c(P)$, and $V(P)$ for HgPb1223. $\kappa_c/\kappa_a = 2.3$ for HgPb1223 follows the trend of $\kappa_c/\kappa_a = 3.0$ for Hg1201,²² but $B_V = 143 \pm 15$ GPa for HgPb1223 is larger by a factor of about 40% than $B_V = 104$ of Hg1201.²² $B_V = 143 \pm 15$ GPa for HgPb1223 is also larger than $B_V = 82.6 \pm 10$ GPa by Eggert *et al.*³⁹ We also pointed out the large discrepancies in the value of the bulk modulus between ours and others as pointed out earlier for other materials by Schilling *et al.*³⁰ The difference may be due to the sample quality, pressure medium, and/or large uncertainties in the data.

We have produced $T_c(V)$ for HgPb1223 from the measured values of $T_c(P)$ and $V(P)$. We have noticed that the pressure derivative of both $T_c(P)$ and $V(P)$ have a smaller value around 2 GPa. This, however, leads to $T_c(V)$ which is *nearly linear* to V (see Fig. 7). The results are shown as $\Delta T_c(V/V_0)$ and compared with others. Although T_c for HgPb1223 increases slower than that for Hg1201 for a given pressure change, T_c for HgPb1223 in-

creases faster than that for Hg1201 for a given change in the normalized volume. Thus three-layer systems appear to boost T_c more than one-layer systems for a given amount of change in the interlayer distance. This conclusion addresses the importance of combining $T_c(P)$ and $V(P)$ to produce $T_c(V)$.

$d \ln T_c / d \ln V$ for HgPb1223 was generated as a function of V/V_0 and was compared with others. $d \ln T_c / d \ln V$ near ambient pressure is about -1.4 which is slightly larger than -1.5 for Hg1201. These values are lower than $d \ln T_c / d \ln V = -1.2$ for the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ as established by Klehe *et al.*¹¹ The major discrepancy between ours and theirs is due to the difference in the bulk modulus used. Due to the large difference in the value of bulk modulus among the literatures, our $d \ln T_c / d \ln V$ was generated without directly using the value of B_V . Based on their result, they concluded that the compounds in the homologous series are electronically (magnetically) similar and the same physical mechanism is responsible for the increase in T_c with pressure. The results of this investigation may call such a conclusion into a question, since we have shown that $d \ln T_c / d \ln V$ for Hg1201 is not exactly the same as that for HgPb1223.

Furthermore, $d \ln T_c / d \ln V$ for HgPb1223 was compared with the model based on the BCS-like theory with a pairing mechanism other than phonon-electron interaction. This model is unable to describe the experimental result even with variation of one input parameter. Further theoretical interpretation may be heeded. 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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