PHYSICAL REVIEW B VOLUME 57, NUMBER 10 1 MARCH 1998-II

Overdoped $Hg_{1-x}Au_xBa_2Ca_2Cu_3O_{8+x}$ and the origin of the intrinsic increase of T_c under pressure in mercury cuprates

C. Acha*
EPM-Matformag and Centre de Recherches sur les Très Basses Températures, CNRS, BP 166, 38042 Grenoble Cedex 9, France

M. Núñez-Regueiro†
EPM-Matformag, CNRS, BP 166, 38042 Grenoble Cedex 9, France

S. Le Floch, P. Bordet, J. J. Capponi, and C. Chaillout
Laboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble Cedex 9, France

J.-L. Tholence
L.E.P.E.S., CNRS, BP 166, 38042 Grenoble Cedex 9, France

(Received 18 November 1997)

We have measured the pressure effect on the superconducting transition temperature T_c of samples of $Hg_{1-x}Au_xBa_2Ca_2Cu_3O_{8+x}$. Even for a high degree of overdoping T_c increases with applied pressure, implying that it is not only the change of charge transfer between the reservoir blocks and the copper oxide planes that enhances T_c. We show here instead that the change of the proximity effect induced by the decrease of the distance between copper oxide blocks can account for the increase of T_c below 10 GPa. [S0163-1829(98)50110-5]

Among all the high-temperature cuprates, the mercury system is the one that presents the most intriguing increase of the superconducting transition temperature, T_c, both for its rate of increase and for the attained values, which correspond to the highest ever observed T_c. The first pressure[1,2] measurements on the Hg-Ba-Ca-Cu-O system in hydrostatic piston-cylinder vessels showed that T_c increased under compression at a rate of 1.7 K/GPa, a strong rate that would correspond to an underdoped sample. However, as soon as optimally doped samples became available, it became evident that this rather strong rate continued to the highest pressures reaching 153 K,[3] 158 K,[4] and finally going through a maximum near 164 K (Ref. 5) at around 30 GPa. Most of the other groups that performed measurements subsequently confirmed this strong increase.[6–10] However, in spite of the efforts to comprehend this phenomenon in order to determine the best route to stabilize the observed high T_c's at ambient pressure, the key to its understanding is still lacking. One still missing piece of information is the high-pressure behavior of overdoped samples of the three layer mercury cuprate, that may clarify the relative importance of charge transfer in the increase of T_c under pressure. In this communication we present measurements on overdoped $(Hg_{1-x}Au_x)$-1223 samples that furnish new light on this issue.

The sample preparation and characterization of the $Hg_{1-x}Au_xBa_2Ca_2Cu_3O_{8+x}$ samples have been described in detail in Ref. 11. The compounds were synthesized by using the high-pressure–high-temperature technique in a belt-type apparatus. Precursors with nominal composition $Ba_2Ca_{n-1}Cu_nO_x$ were prepared from a mixture of oxides and nitrates, followed by annealing at temperatures between 900 and 925 °C for 72 h under an oxygen flow. The precursors were then mixed with an appropriate amount of gold and mercury oxides, and submitted to the high-pressure–high-temperature treatment at 1.8 GPa and 950 °C for 1.6 h. The samples obtained were characterized by x-ray powder diffraction, high-resolution electron microscopy, and energy dispersive spectroscopy analysis using a Philips CM300 in the TEM.

High-pressure resistance measurements (HPR) were performed with the Bridgman sintered diamond anvil configuration used in Ref. 4 in quasihydrostatic conditions, on powder extracted from ceramic samples. Steatite was used as the pressure transmission medium and pyrophillite as a gasket. Pressure was estimated by means of the superconducting transition of lead and the resistance was measured using a standard four contact dc technique. The sample's current densities ranged from 0.1 to 10 A/cm^2. We show in Fig. 1 typical resistivity temperature dependencies measured on our samples. Possibly due to deterioration during grinding, the superconductivity only percolates completely at low temperatures. Some of the samples also showed two distinct superconducting transitions, both in the susceptibility and resistivity measurements, which correspond to gold doping inhomogeneities. This behavior was retained by the powder that was introduced in the pressure cell. We present in Fig. 2 the pressure dependence of the superconducting transition temperature for several samples of different nominal concentration. T_c was determined by the peak of the derivative of the resistance as a function of temperature. It is interesting to note the increase of T_c with pressure, even for the highly overdoped ones.

We can analyze our results in the light of a straightforward formulation of the change of T_c with pressure[12–14] supposing that we have essentially two effects: the variation of

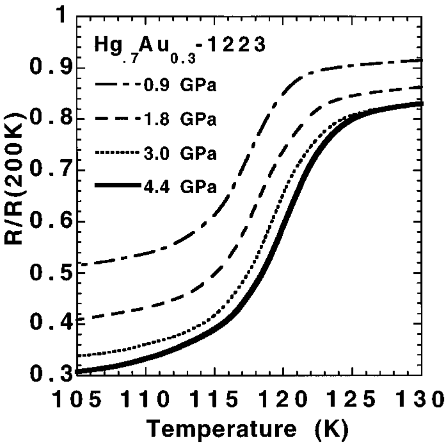

FIG. 1. Temperature dependence of the resistance, normalized to its value at 200 K, of a Hg$_{0.7}$Au$_{0.3}$-1223 sample as a function of pressure.

carrier transfer dn/dP and an intrinsic T_c change independent of charge transfer, dT_c^i/dP. Let us assume a linear dependence on pressure for $n(P)$ and considering the general expression $T_c(n)=T_c^{\max}(P)[1-\eta(n_{\mathrm{op}}-n)^2]$ we arrive at the following equations for $T_c(n,P)$:

$$T_c(n,P)=T_c(n,0)+\alpha(n)P+\beta(n)P^2, \tag{1}$$

with

$$\alpha(n)=dT_c^i/dP+2\,\eta T_c^{\max}dn/dP(n_{\mathrm{op}-n}), \tag{2}$$

and

$$\beta(n)=-\,\eta T_c^{\max}(dn/dP)^2, \tag{3}$$

where $T_c^{\max}$ is the maximum T_c obtained with doping for $P=0$, n_{op} the optimal doping, and η a constant related to n_{op} and to the minimum doping for obtaining a superconducting state.

We show in Fig. 2 the fits we obtain with expression (1) that allow us to extract an estimation of the doping level of the samples (shown between brackets in Fig. 2). If the only oxygens present in the reservoir planes are the two fixed per gold ion, the hole concentration should coincide with the gold concentration. The deduced values suggest that more oxygen is present in the 0.1 sample. For the other samples, different mechanisms of doping, such as formation of Au-O chains, must be invoked to explain the lower than expected obtained values.

On the other hand, as any increase in an overdoped sample cannot be attributed to a charge transfer, only an intrinsic effect under pressure can explain our results. Even our well overdoped samples continue to increase their T_c under compression. A similar strong intrinsic effect evidenced by an increase of T_c in overdoped samples has also been observed for Hg-1201,[15] indicating that it is a common feature of Hg- 1:2:(n−1):n compounds. Also the two mercury layer material Hg$_2$Ba$_2$(Y$_{1-x}$Ca$_x$)Cu$_2$O$_{8-y}$ has shown[16] an extremely large linear increase in T_c that can only be attributed to an intrinsic effect. It is thus important to look for a common structural variation under pressure for mercury cuprates.

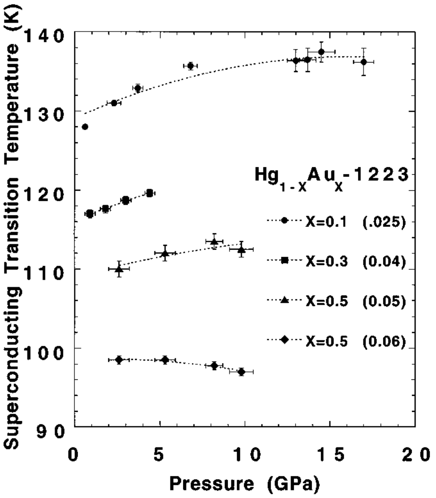

FIG. 2. Pressure dependence of the superconducting transition temperature T_c of several Hg$_{(1-x)}$Au$_x$-1223 samples. On the legend the x values correspond to the nominal gold concentration. The values in parentheses are the excess carrier concentrations, with respect to the optimal doping concentration, calculated from the fit of expression (1).

HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ band structural calculations have been done essentially for two x concentrations: $x=0$ (Refs. 17 and 18) (no oxygen in the mercury plane) or for an occupation number $x=0.5$ (Ref.19) (in an ordered array). In the first case there is an antibonding band coming mostly from the hybridization of Hg-p and d-(apical oxygens) O-p states, that crosses the Fermi level and is partly responsible for the doping of the Cu-O bands in the CuO$_2$ layers. The observed increase with pressure of T_c has been attributed to an increase of charge transfer between these two bands that pulls a van Hove anomaly towards the Fermi level.[20] However, this approach is not easily harmonized with the increase of T_c in the overdoped samples that we observe. In the second case, there is formation of an antibonding Hg-p-(in plane) O-p band which, being slightly empty, yields a charge transfer from the Hg-O unit to the CuO$_2$ planes that is smaller than the one expected from purely ionic considerations. Furthermore, a negligible pressure-induced charge transfer is theoretically predicted[21] in accordance with our measurements.

We now analyze the structural changes that have been measured under pressure to try to determine the possible causes for the existence of this strong intrinsic term. The structural changes with pressure[22] show that the almost flat CuO$_2$ planes (α=177.4°) in the starting Hg-1223 material are buckled by pressure (α=173.7°). An analogous behavior is measured[23] in Hg-1212. Empirically we would expect a reduction of T_c by this buckling which is known to be detrimental to superconductivity, as can be clearly seen from pressure experiments in the La$_{(2-x)}$Ba$_x$CuO$_4$ system.[24] As an increase of T_c is observed, this effect should be less important than the main one, which dominates the $T_c(P)$ dependence.

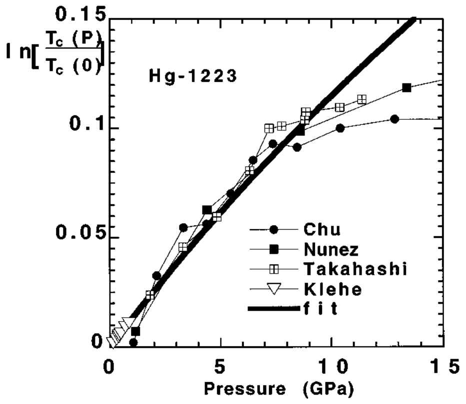

FIG. 3. Comparison of the one parameter fit of expression (6) to the normalized T_c's obtained by different groups[3,4,9,6] on Hg-1223.

Another important structural variation[22] under pressure is the following: the separation between the three CuO_2 planes of the same blocks changes less than 1% while the distance between different three layered CuO_2 blocks varies almost 10% between ambient pressure and ~10 GPa. We can consider our compound as an intrinsic multilayer composed of three superconducting (s) CuO_2 blocks and metallic (n) HgO reservoirs (according to band calculations), of thickness $d_s \sim 6.25$ Å and $d_n \sim \mathbf{c}$-6.25 Å, respectively. Within this picture, and considering that pressure-induced charge transfer is low, the principal effect of pressure is to reduce d_n. The variation of d_n with pressure is mainly due to the variation of the lattice parameter **c**.

In a simplified proximity effect framework, the superconducting pairs sample an effective attractive potential ($V_{\rm eff}$) which is the spatial average of the potentials in each side of the s/n interface. Then, according to the early theories of Cooper,[25] Werthammer,[26] and deGennes,[27] we can calculate the superconductor transition temperature (T_c) using a BCS formula.

$$\begin{aligned} T_c &= 1.14\theta \exp\left\{-\frac{1}{[N(0)V]_{\rm eff}}\right\} \\ &= 1.14\theta \exp\left\{-\frac{d_s+d_n}{d_s[N(0)V]_s}\right\}, \end{aligned} \tag{4}$$

where θ is the characteristic energy of the virtual bosons exchanged by the paired electrons ($\Theta_{\rm Debye}$ for electron-phonon superconductivity) and $N(0)$ is the electronic density at the Fermi level.

It is assumed that in the nonsuperconducting layer $[N(0)V]_n = 0$ and that the superconducting (ξ_s) and the metallic (ξ_n) coherence length are larger than d_s and d_n, respectively. From superlattices experimental results, the limit $\xi_n > d_n$ is clearly verified.[28] Although the measured[29] $\xi_{ab} \sim 20$ Å satisfies this criterion, ξ_c can be four times smaller. In the limit where $d_s \gg \xi_s$ and $d_n > \xi_n$, T_c could also be described[27] by an exponential law of the form $T_c = T_{\rm lim} + A \cdot \exp(-Bd_n)$, with $A,B > 0$. Thus, the expressions obtained for both limits indicate a net enhancement of T_c with pressure.

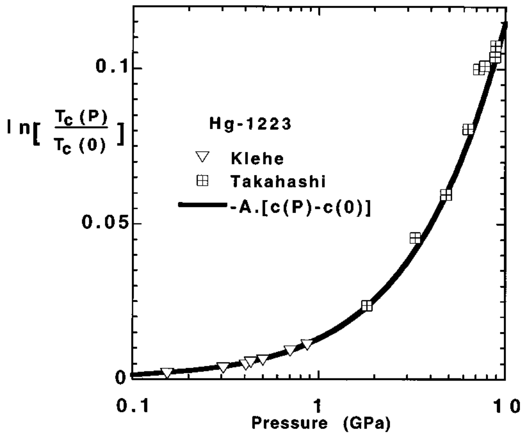

FIG. 4. Logarithmic plot of the one parameter fit of expression (6) to the data of Refs. 6 and 9 obtained in hydrostatic conditions showing the excellent accord obtained for two decades in the pressure range.

As the pressure dependence of the **c** parameter has been measured precisely, $\mathbf{c}(P)$ can be fitted[30] using known equations of state; we find then from Eq. (4) for the transition temperature as a function of pressure

$$T_c(P) = 1.14\theta(P)\exp\left\{-\frac{c(P)[N(0)V]_s}{6.25}\right\}, \tag{5}$$

which can also be expressed as

$$\ln\left[\frac{T_c(P)}{T_c(0)}\right] = -\frac{[N(0)V]_s}{6.25}[c(P)-c(0)], \tag{6}$$

assuming as unimportant the pressure variations of the characteristic energy θ, the superconducting interaction V, and the electronic density at the Fermi level $N(0)$. Band structure calculations[21] in the Hg-1223 compound are in accordance with the latter assumption as they show a very small variation of $N(0)$ with pressure.

We show in Fig. 3 data from different groups together with the fit from Eq. (6). The agreement is excellent with only one parameter, $A = (1.00 \pm 0.02)/6.25$. At pressures higher than 10 GPa (not shown in the figure[31]) all the samples follow curves lower than the one calculated from expression (6), and the behavior becomes very sample dependent. A detailed analysis of the published experimental data shows that, as expected, the data obtained in hydrostatic apparatus follow a more systematic behavior. We show in Fig. 4 that the *one parameter fit* of Eq. (6) also agrees accurately with these data *for two decades* in the pressure range.

We have thus shown that the large T_c increase observed in Hg-1223 materials can be just the result of an improved coupling between CuO_2 blocks induced by the contraction under pressure of the reservoir Hg layers. According to this conclusion, in order to stabilize at ambient pressure the high T_c observed in Hg-1223 under pressure, chemical substitutions should be aimed essentially at reducing the separation between the CuO_2 blocks, without altering the CuO_2 layers.

C.A. would like to thank the Consejo Nacional de Investigaciones Cientificas y Tecnicas of Argentina for financial support.

---

*Present address: Laboratorio de Bajas Temperaturas, Depto. de Física-FCEyN-UBA, Ciudad Universitaria, PAB I, (1428) Buenos Aires, Argentina.

†Author to whom correspondence should be addressed. Electronic address: nunez@labs.polycnrs-gre.fr

[1] L. Gao, Z. J. Huang, R. L. Meng, J. G. Lin, F. Chen, L. Beauvais, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Physica C **213**, 261 (1994).

[2] A. K. Klehe, A. K. Gangopadhyay, J. Diederichs, and J. S. Schilling, Physica C **213**, 266 (1993).

[3] C. W. Chu, L. Gao, F. Chen, Z. J. Huang, R. L. Meng, and Y. Y. Xue, Nature (London) **365**, 323 (1993).

[4] M. Núñez-Regueiro, J. L. Tholence, E. V. Antipov, J. J. Capponi, and M. Marezio, Science **262**, 97 (1993).

[5] L. Gao, Y. Y. Xue, F. Chen, Q. Xiong, R. L. Meng, D. Ramirez, and C. W. Chu, Phys. Rev. B **50**, 4260 (1994).

[6] A. K. Klehe, J. S. Schilling, J. L. Wagner, and D. G. Hinks, Physica C **223**, 313 (1994).

[7] F. Chen, L. Gao, R. L. Meng, Y. Y. Hue, and C. W. Chu, J. Appl. Phys. **76**, 6941 (1994).

[8] Y. S. Yao, Y. J. Su, W. Liu, H. Gong, J. W. Li, G. H. Cao, F. Wu, and Z. X. Zhao, Physica C **224**, 91 (1994).

[9] H. Takahashi, A. Tokiwa-Yamamoto, N. Môri, S. Adachi, H. Yamauchi, and S. Tanaka, Physica C **218**, 1 (1993).

[10] M. Kosuge, A. Tokiwa-Yamamoto, H. Yamauchi, and N. Koshizuka, Physica C **225**, 218 (1994).

[11] P. Bordet, S. LeFloch, J. J. Capponi, M. F. Gorius, M. Marezio, J. L. Tholence, and P. G. Radaelli, Physica C **262**, 151 (1996).

[12] C. C. Almasan, S. H. Han, B. W. Lee, L. M. Paulius, M. B. Maple, B. W. Veal, J. W. Downey, A. P. Paulikas, Z. Fisk, and J. E. Schirber, Phys. Rev. Lett. **69**, 680 (1992).

[13] J. J. Neumeier and H. A. Zimmermann, Phys. Rev. B **47**, 8385 (1993).

[14] R. P. Gupta and M. Gupta, Phys. Rev. B **51**, 11 760 (1995).

[15] Y. Cao, Q. Xiong, Y. Y. Hue, and C. W. Chu, Phys. Rev. B **52**, 6854 (1995).

[16] C. Acha, S. Loureiro, C. Chaillout, J.-J. Capponi, J.-L. Tholence, M. Marezio, and M. Núñez-Regueiro, Solid State Commun. **102**, 1 (1997).

[17] C. O. Rodríguez, N. E. Christensen, and E. L. Peltzer y Blancá, Physica C **216**, 12 (1993).

[18] D. L. Novikov and A. J. Freeman, Physica C **216**, 273 (1993).

[19] D. J. Singh and W. E. Pickett, Phys. Rev. Lett. **73**, 476 (1994).

[20] D. L. Novikov, O. N. Mryasov, and A. J. Freeman, Physica C **222**, 38 (1994).

[21] D. J. Singh and W. E. Pickett, Physica C **233**, 237 (1994).

[22] A. R. Armstrong, W. I. F. David, J. S. Loveday, L. Gameson, P. P. Edwards, J. J. Capponi, P. Bordet, and M. Marezio, Phys. Rev. B **52**, 15 551 (1995).

[23] B. A. Hunter, J. D. Jorgensen, J. L. Wagner, P. G. Radaelli, D. G. Hinks, H. Shaked, and R. L. Hittermand, Physica C **221**, 1 (1994).

[24] N. Môri, M. Takai, A. Tomiaoka, S. Ogawa, Y. Ueda, H. Takahashi, and S. Katano, J. Supercond. **7**, 462 (1994).

[25] L. N. Cooper, Phys. Rev. Lett. **6**, 89 (1961).

[26] N. Werthammer, Phys. Rev. **132**, 2440 (1963).

[27] P. G. deGennes, Rev. Mod. Phys. **36**, 225 (1964).

[28] J. Z. Wu, C. S. Ting, W. K. Chu, and X. X. Yao, Phys. Rev. B **44**, 411 (1991); I. N. Chan, D. C. Vier, O. Nakamura, J. Hasen, J. Guimpel, S. Schultz, and I. K. Schuller, Phys. Lett. A **175**, 241 (1993).

[29] R. Puzniak, R. Usami, K. Isawa, and H. Yamauchi, Phys. Rev. B **52**, 3756 (1995).

[30] J. H. Eggert, J. Z. Hu, H. K. Mao, L. Beauvais, R. L. Meng, and C. W. Chu, Phys. Rev. B **49**, 15 299 (1994).

[31] See, for instance, Fig. 6 of D. Tristan Jover, R. J. Wijngaarden, H. Wilhelm, R. Griessen, S. M. Loureiro, J.-J. Capponi, A. Schilling, and H. R. Ott, Phys. Rev. B **54**, 4265 (1996).