Hydrostatic pressure on $HgBa_2CaCu_2O_{6+\delta}$ and $HgBa_2Ca_2Cu_3O_{8+\delta}$

F. Chen, L. Gao, R. L. Meng, Y. Y. Xue, and C. W. Chu
Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5932

The superconducting transition temperature T_c and its pressure dependence dT_c/dP of $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) were measured up to 17 kbar. T_c increases with pressure approximately linearly for both compounds before oxidation. However, the nonlinearity in the T_c-P correlation shows up after oxidation in both compounds. For Hg-1212, the average dT_c/dP decreases as oxygen doping increases, while it increases in Hg-1223. These observations are in conflict with the modified pressure-induced charge-transfer model, but might be attributed to the possible existence of fine electronic structure. These observations suggest that a T_c much higher than 140 K might be achievable in Hg-1223 by means of higher physical or chemical pressure.

I. INTRODUCTION

Previous pressure studies on high T_c cuprates at various oxidation states show that the T_c changes linearly at pressures between 0 and 20 kbar.[1] This can usually be explained by pressure-induced charge-transfer,[2] i.e., dT_c/dP decreases with the carrier concentration n, which increases with oxidation. Soon after the discovery of the superconducting homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [Hg-12(n-1)n],[3] band-structure calculations showed that the electronic structure of these compounds was strongly affected by the van Hove singularity and evolved with doping rather abnormally,[4] suggesting that their pressure effect dT_c/dP might be unusual. After samples of these compounds with different oxygen stoichiometry became available, we systematically studied their pressure dependence.

A positive dT_c/dP was observed in all $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) samples. For the as-prepared Hg-1212 samples with $T_c \sim 112$ K, T_c increased linearly with pressure at a rate $dT_c/dP = 0.22 \pm 0.02$ K/kbar throughout our pressure range. For oxygenated Hg-1212 samples with $T_c \sim 119$ K, T_c increases with pressure at a similar rate below ~4 kbar, but the rate of increase decreases to 0.11 ± 0.02 K/kbar thereafter. Although the nonlinear T_c-P correlation is rather unusual, the smaller average dT_c/dP after oxygenation is consistent with the charge-transfer model,[2] which suggests that the average dT_c/dP decreases with the carrier concentration n. The dT_c/dP of several Hg-1223 samples was also measured. The dT_c/dP of vacuum-annealed and as-synthesized samples was independent of P. However, the T_c vs P of oxygenated Hg-1223 shows positive curvature above 12 kbar. Unlike that for Hg-1212, the overall dT_c/dP for Hg-1223 increases with oxidation, which is in direct conflict with the modified charge-transfer model.[2]

II. EXPERIMENT

High quality samples were prepared using the controlled vapor/solid reaction (CVSR) technique.[5] The samples are ~90% pure with ~10% $CaHgO_2$ and $Ba_2Cu_3O_{5+\delta}$ impurities. Structure characterization was carried out by x-ray diffraction using a Rigaku D-MAX/BII powder diffractometer. The dc magnetic susceptibility (χ_{dc}) of samples at ambient pressure was measured by a quantum design superconducting quantum interference device (SQUID) magnetometer. A standard inductance bridge, operated at 16 Hz in an ac field of ~5 Oe peak to peak, was employed to determine the ac magnetic susceptibility (χ_{ac}) under pressures. The standard four-lead measurement was applied to measure resistivity. Hydrostatic pressure up to 18 kbar was generated at room temperature inside a Teflon cup housed in a Be-Cu high pressure clamp,[6] using 3M Fluorinert as the pressure medium. The pressure was determined by a Pb-manometer placed next to the sample. The temperature was measured by an alumel-chromel thermocouple above 30 K and a Ge thermometer below 30 K.

III. RESULTS AND DISCUSSION

Four samples of Hg-1212 were characterized. Samples A and C were as synthesized with $T_c \sim 112$ K. Samples B and D were annealed in 1 atm O_2 at 300 °C for 30 h with $T_c \sim 119$ K and were determined to be overdoped. The χ_{dc} of samples A, B, and D are shown in Fig. 1. The transition is quite sharp and the superconducting volume fraction is large (especially for sample D). The onset and midpoint of T_c(T_{co} and T_{cm}) as determined by ac-susceptibility measurements at various pressures are shown in Fig. 2. The T_{co}'s of sample A and C have the same trend as the T_{cm}'s although they are not shown in the figure. The T_{cm} of sample D is not well defined due to poor grain coupling and thus not shown. T_c increases linearly with P at a rate of 0.22 ± 0.02 K/kbar for samples A and C. For samples B and D, T_c increases at a rate of ~0.23 K/kbar below 4 kbar. The rate fell to 0.11 ± 0.03 K/kbar above 4 kbar. As proposed by the modified charge-transfer model,[2] the overall dT_c/dP decreases as oxidation increases.

Five samples from two different batches of Hg-1223 were also examined. Sample V was as synthesized with $T_c \sim 117$ K. Sample W, with $T_c \sim 79$ K, was obtained by high vacuum annealing at 450 °C for 1 day. Samples X, Y, and Z were annealed in flowing oxygen at 300 °C for 1 day, with $T_c \sim 135$ K. Figure 3 shows T_c versus pressure for Hg-1223. The T_c's for samples V, X, Y, and Z were measured resistively. Although we only plotted T_{cm} for these samples, the behavior of T_{co} and T_{cz} (zero point of the transition) is similar. A long tail in the superconducting transition was ob-

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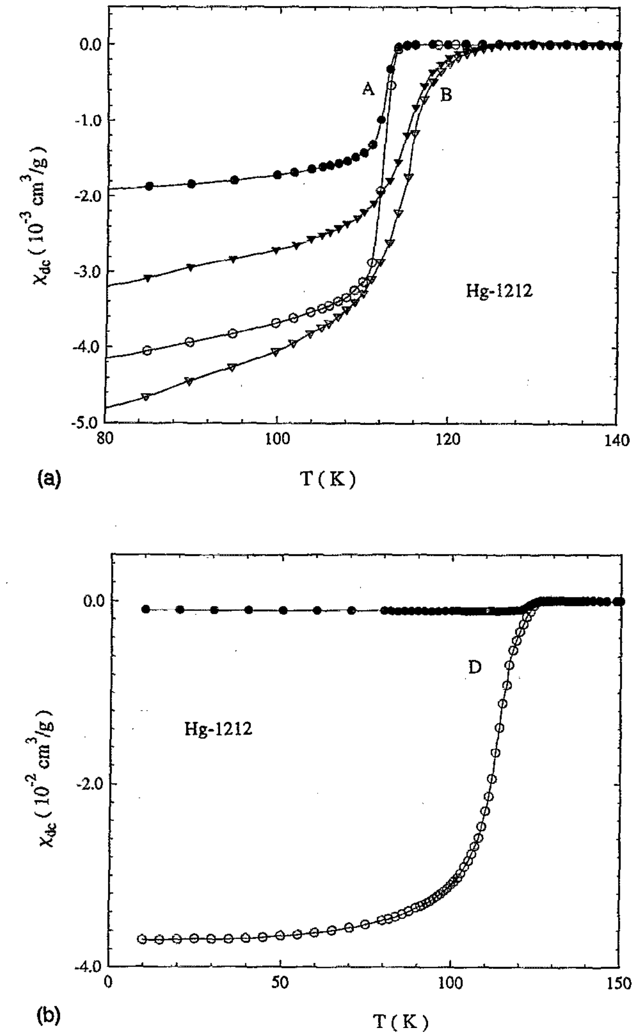

FIG. 1. (a) χ_{ac} vs T for Hg-1212 sample A and B. (b) χ_{dc} vs T for Hg-1212 sample D. Filled symbol: field cooling; open symbol: zero-field cooling.

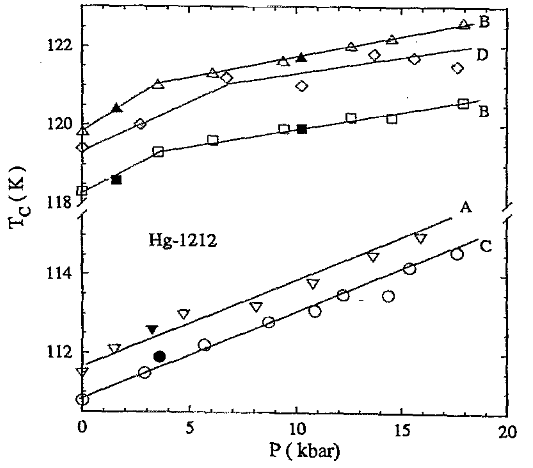

FIG. 2. T_c vs P for Hg-1212. △: T_{co} for sample B; ◇: T_{co} for sample D; □: T_{cm} for sample B; ▽: T_{cm} for sample A; ○: T_{cm} for sample C. Filled symbol obtained on pressure reduction.

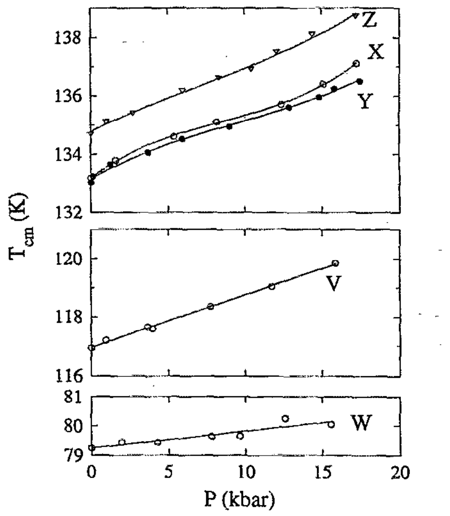

FIG. 3. T_{cm} vs P for Hg-1223 samples V, W, X, Y, and Z.

served for the sample W, which might be due to damage caused to the grain boundaries during annealing. Therefore, the T_c of this sample was measured magnetically and T_{cm} was obtained from the peak of $d\chi_{ac}/dT$. We can see clearly that the average dT_c/dP increases with oxidation. From thermoelectric measurements, we extracted the carrier concentration n by an empirical law.[7] Figure 4 shows the average dT_c/dP vs n for Hg-1212 and Hg-1223.

Recently, a study[2] of combined effects of pressure and doping on $(Y,Ca)(Ba,Ca)_2Cu_3O_{7-\delta}$ compounds shows that pressure-induced charge-transfer alone cannot explain the observed results and an "intrinsic" pressure effect on T_c is included. This term, $dT_{c,\max}/dP$, is assumed to be independent of P and n. Thus, the empirical modified pressure-induced charge-transfer model can be written as

$$T_c(n,P)=T_{c,\max}(n_{\text{optimal}},0)+(dT_{c,\max}/dP)\times P +A\times[(n-n_{\text{optimal}})+(dn/dP)\times P]^2,$$

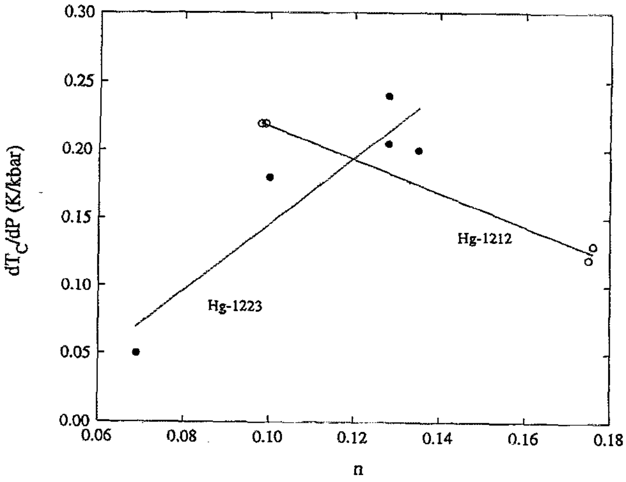

FIG. 4. dT_c/dP vs n for Hg-1212 and Hg-1223.

where A is a negative compound-dependent constant. By ignoring higher order contributions, the pressure effect on T_c becomes

$$dT_c/dP = dT_{c,\max}/dP + 4A \times dn/dP \times (n - n_{\text{optimal}}),$$

which should decrease with n (oxidation), since $dn/dP > 0$ (which has been demonstrated by the negative $d\rho/dP$, positive dR_H/dP;[8] where ρ is normal state resistivity and R_H is the Hall coefficient). However, the average dT_c/dP increases with n in Hg-1223, despite the negative $d\rho/dP$ over the whole P range. This is in direct conflict with the model[2] and suggests that $dT_{c,\max}/dP$ should be P and/or n dependent. The ever increasing dT_c/dP with P after oxidation (cf. Fig. 3) suggests that the T_c of Hg-1223 can be enhanced further by applying pressures up to 500 kbar.[9]

In summary, we investigated the pressure effect on samples of Hg-1212 and Hg-1223 with different oxygen contents. We found that the pressure effect becomes rather nonlinear after oxidation. Although a modified charge-transfer model can explain the pressure effect on Hg-1212, it is in direct conflict with the observation on Hg-1223. The positive dT_c/dP for all the samples suggests that high T_c is optimistic.

ACKNOWLEDGMENTS

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