High Pressure Study of The T$_c$ and Thermopower of Hg-based Cuprates

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The pressure effects on superconducting transition temperature T_c and thermopwer S were studied up to 16 GPa for $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$ with m = 1–3 over a broad doping range. Direct measurement for a $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$ sample with T_c = 115 K shows that the charge transfer is negative and unusually small, *i.e.* ~ -0.0004 holes/($\mathrm{CuO_2}$·GPa). The T_c (P) over a broad doping levels, on the other hand, suggests that factors not being considered in the charge transfer model may play important roles. Site-selective cation-substitution shows that the local environment of Hg may be one of the factors.

1 Introduction

The charge-transfer induced by pressure P^1 and the van Hove singularity[2] have been used to interpret the large T_c-enhancement under pressure in $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$, but contradictions exist[3]. To clarify the situation, $T_c(P)$ was measured up to 16 GPa over a broad n-range, and $\mathrm{d}n/\mathrm{d}P$ was deduced from the measured $\mathrm{d}S/\mathrm{d}P$, where n is the carrier density and S is the thermopower. Our data demonstrate not only that the $\mathrm{d}n/\mathrm{d}P$ of $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$ is too small to contribute significantly to the T_c-enhancement, but also that other factors not being considered before may play important roles. We observed that the T_c-enhancement is very sensitive to substitutions at the Hg-site, suggesting the local environment of Hg is one of the factors.

2 Experiments

All samples were single phase polycrystalline with a sharp superconducting transition. Instruments for providing quasi-hydrostatic pressure (QHP) up to 18 GPa and hydrostatic pressure up to 1.6 GPa were reported before.[3,4] The thermopower was measured using a homemade apparatus[5] designed to reduce the pressure-medium effects. The pressure effects of the p-Chromel/Cu thermocouples, which were used to measure the temperature gradient across the sample, was calibrated.

3 Data and Discussion

The traditional charge transfer models[1] obtain $\mathrm{d}T_c/\mathrm{d}P = \mathrm{d}T_c^{max}/\mathrm{d}P$-$2\alpha(n - n^{op})\cdot(\mathrm{d}n/\mathrm{d}P)$ from the proposed $T_c = T_c^{max}$ $[1$-$\alpha(n - n^{op})^2]$, and assume that both $\mathrm{d}T_c^{max}/\mathrm{d}P$ and $\mathrm{d}n/\mathrm{d}P$ are independent of P and n, where α and n^{op} are universal constants. Therefore, $\mathrm{d}n/\mathrm{d}P = -(\partial^2 T_c/\partial P \partial n)/(2\alpha)$ can be deduced from the n-dependence of $\mathrm{d}T_c/\mathrm{d}P$. $\mathrm{d}n/\mathrm{d}P$ of $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$ so obtained has been given previously as $\sim 0 \pm 0.0001$,[6] $+0.0008$,[4] and -0.0013 holes/($\mathrm{CuO_2}$·GPa)[7] for m = 1, 2 and 3 respectively (Inset of Fig. 1). These values are rather small, *e.g.*, about one tenth of the $\mathrm{d}n/\mathrm{d}P \sim 0.011$ holes/($\mathrm{CuO_2}$·GPa) in $\mathrm{YBa_2Cu_3O_{7-\delta}}$.[8] However, these small $\mathrm{d}n/\mathrm{d}P$ still contributes a significantly m-dependent term of $-\alpha T_c^{max}(P\cdot\mathrm{d}n/\mathrm{d}P)^2$, ~ 0, -7 and -15 K at 30 GPa for m = 1, 2 and 3 respectively, following the model in Ref. 1. Such predicted m-dependence seems to be too large based on the observed $\Delta T_c = T_c(P) - T_c(0)$, which is m-independent within 3 K (Fig. 1). Therefore, a direct measurement of $\mathrm{d}n/\mathrm{d}P$ is desired.

Figure 1: Universal ΔT_c *vs* pressure for optimal doped $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$. Inset: $\mathrm{d}T_c/\mathrm{d}P$ *vs* hole concentration for $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$.

Figure 2: Thermopower raw data near room temperature under pressure for $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$ ($T_c = 115$ K).

We deduced $\mathrm{d}n/\mathrm{d}P$ by measuring the thermopower S under pressure. It has been suggested that n *vs* S at 290 K obeys a universal trend in cuprates.[10] The proposed correlation has been tested in $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$ with m = 1–3 at the ambient pressure.[5] $\mathrm{d}n/\mathrm{d}P$ can be deduced, therefore, from $\mathrm{d}S(290\,\mathrm{K})/\mathrm{d}P$ if the proposed universal S *vs* n trend is hold under pressure. It should be note that a change of n usually causes a significant change of S in most metal and semiconductors where the proposed S *vs* n universality is not valid. An underdoped $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$ with $T_c \sim 115$ K was measured under hydrostatic pressure up to 1.6 GPa. Two Cu/p-Chromel thermocouples were used to measure the temperature difference ΔT with the Cu-wires also serving as the voltage leads. The thermopower raw data $S^{raw}(P)$ calculated assuming $S_{p-Chromel}(P) = S_{p-Chromel}(0)$ and $S_{Cu}(P) = S_{Cu}(0)$, will be related to the actual $S(P)$ as $[S^{raw}(P) - S_{Cu}(0)]/[S_{p-Chromel}(0) - S_{Cu}(0)] = [S(P) - S_{Cu}(P)]/[S_{p-Chromel}(P) - S_{Cu}(P)]$, where $S(P)$, $S_{p-Chromel}(P)$ and $S_{Cu}(P)$

are the thermopowers of the sample, p-Chromel and Cu under pressure respectively. The observed S^{raw} shifted parallel with the pressure (Fig. 2). The random data-scattering was better than 10 nV/K or 0.00002 holes/CuO$_2$, and $S_{Cu}(P) \approx S_{Cu}(0)$ is a good approximation. However, a large systematic uncertainty may be caused by $S_{p-Chromel}(P) - S_{Cu}(P)$. By carefully calibrating $S_{p-Chromel}(P) - S_{Cu}(P)$ against two Pt-thermometers, we reduce the total uncertainty to < 0.3 μV/(K·GPa) or 0.0007 holes/GPa.

The deduced dn/dP of the HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples is -0.0004 ± 0.0007 holes/(CuO$_2$·GPa) using the universal $S(290)$ *vs* n trend. Although this value is not directly in contrast to that of ~ -0.0013 holes/(CuO$_2$·GPa) obtained from the charge transfer model, the smaller value of -0.0004 seems to be more reasonable based on the observed universal $\Delta T_c(P)$. This may suggest that the actual charge transfer is not even equal to $-(\partial^2 T_c/\partial P \partial n)/(2\alpha)$ if further investigations confirm our results.

dn/dP of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ has been calculated theoretically. Novikov[2] gave a rather large value of 0.027 holes/(CuO$_2$·GPa) over 0–9.4 GPa and Singh[11] reported a dn/dP = 0.0022 holes/(CuO$_2$·GPa). Both results are in disagreement with our data and further investigations are needed. Such negligible dS/dP can neither be accommodated with the proposed van Hove singularity.[2] S should change drastically when the Fermi surface approaches a singularity, which is in direct contrast with our data.

Figure 3: Isobaric plot of T_c *vs* carrier concentration for HgBa$_2$CuO$_{4+\delta}$. Inset: dT_c/dP for HgBa$_2$CuO$_{4+\delta}$ with different δ.

Figure 4: T_c *vs* QHP for HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (◯), (Hg$_{0.8}$Pb)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (△) and Hg(Ba$_{0.75}$Sr$_{0.25}$)$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (□).

To further verify the charge transfer models, T_c of HgBa$_2$CuO$_{4+\delta}$ was measured up to 16 GPa over a broad n range (Fig. 3). The isobaric T_c *vs* δ plot will only parallel shift with P, *i.e.* only T_c^{max} changes, under the charge transfer model[1] and accepting dn/dP ~ 0 as we have demonstrated. Although our data (Fig. 3) can be reasonably fitted with $T_c = T_c^{max} \cdot [1 - \beta(\delta - \delta^{op})^2]$, all three parameters T_c^{max}, δ^{op} and β vary with P. The value of β, for example, increases nearly 50% with P up to 16 GPa. The obtained d(δ^{op})/d$P \sim -0.002$ oxygen/(CuO$_2$·GPa), which $\propto$ d$(n^{op} - n)$/dP, is also too large to be accommodated with the observed dn/dP, suggesting a large negative

$\mathrm{d}n^{op}/\mathrm{d}P$ as proposed by us before.[3] These observations suggest that many factors not being considered in the charge transfer models play important roles in the pressure effects in $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$.

To explore these factors, substitutions were carried out at the Ba and Hg sites for $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$. The optimal T_c at ambient pressure changed with these substitutions only moderately, *i.e.* ~ -2 K with 20% substitution of Hg by Pb and ~ -8 K with 25% substitution of Ba by Sr. However, the pressure effects of these substitutions were very different. The maximum T_c-enhancement under pressure in the Pb-substituted samples is only half of that of pure $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$ (Fig. 4). On the other hand, the enhancement remains almost unchanged, or even increases slightly with the Sr-substitution. Therefore, we relate the unusual pressure effects to the local environment of Hg, especially the linear coordination of O-Hg-O.

4 Conclusion

In conclusion, both T_c and S were measured for $\mathrm{HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}}$ at various doping levels. The results show that the charge transfer induced by pressure is very small and has negligible contribution to the T_c-enhancement under pressure. However, many factors not being considered in the charge-transfer models may play important roles. One of the factors may be the local environment of Hg.

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